BBL *Sciences*

Transmitted Via Federal Express

January 30, 2003

Mr. Nabil Fayoumi
U.S. Environmental Protection Agency
Superfund Division
77 West Jackson Blvd (SR-6J)
Chicago, IL 60604

Re: Response to Comments on Quality Assurance/Sampling and Analysis Project Plan
BBL Project #: 10284.001 #2

Dear Mr. Fayoumi:

Enclosed is a comment/response package relating to Mr. Byvik's 14 January 2003 comments on the draft Sauget Area 1 EE/CA-RI/FS Quality Assurance/Sampling and Analysis Project Plan (QA/SAPP). As we have done in the past, we are submitting only our responses to the comments, plan revisions, and specified plan components not included in the prior draft (not the revised QA/SAPP itself). When Solutia, Inc. and USEPA are agreed on the QA/SAPP revisions (after you have a chance to review the responses, revisions, and additions), we will modify the QA/SAPP and submit it to you as a final document.

Please note that we have addressed all of Mr. Byvik's comments, and have added items identified in his review, including a Quality Management Plan for BBL, Inc. (lead contractor for the sampling activities), laboratory identification and SOPs, a project organization chart, signature pages, project timeline, extensive text addressing the DQO process, and other Plan components.

If you have any questions, please contact Richard Williams of Solutia at 618-482-6340.

Sincerely,

BLASLAND, BOUCK & LEE, INC.

David F. Ludwig, Ph.D.
Principal Ecologist

DFL/krm
Enclosure

cc: Distribution

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REPORT

Response to USEPA Comments on Quality Assurance/Sampling and Analysis Project Plan

Sauget Area 1 Dead Creek Sediment Removal Action Mitigation Plan

Solutia, Inc.
Sauget, Illinois

January 2003

BBL®
BLASLAND, BOUCK & LEE, INC.
engineers & scientists

TECHNICAL REPORT

Response to USEPA Comments on Quality Assurance/Sampling and Analysis Project Plan

Sauget Area 1
Dead Creek Sediment Removal Action Mitigation Plan

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Response to USEPA Comments on Quality Assurance/Sampling and Analysis Project Plan, Sauget Area 1, Dead Creek Sediment Removal Action Mitigation Plan

As per Solutia's request, BBL Sciences has responded to the USEPA comments received from Mr. Richard Byvik dated January 14, 2003 on the Draft Quality Assurance/Sampling and Analysis Project Plan (QA/SAPP). Below are the comments from Mr. Byvik; following each of his comments is BBL's response in italics and the changed text from the revised QA/SAPP. If you have any questions or concerns, please do not hesitate to contact us at 410-295-1205.

GENERAL COMMENTS

- Superfund QAPPs must be prepared according to the REGION 5 INSTRUCTIONS ON THE PREPARATION OF A SUPERFUND DIVISION QAPP Revision 0, June 2000.

  Region 5 Instructions were used in the preparation of this QA/SAPP and this has been noted in the Preface of the QA/SAPP along with the other guidance documents considered in the preparation of this document.

  > USEPA Region 5 guidance document entitled "Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan," Revision 0 June 2000.

- **Solutia** must provide a Quality Management Plan. Also, a site Health and Safety Plan should have been prepared and made available.

  BBL, Inc. has provided a Quality Management Plan as Attachment A to the QA/SAPP (Attached.) A Health and Safety Plan has been prepared and has been made available to the USEPA. The text of Section 2, Project Background, has been revised as follows:

  > The applicable Health and Safety Plan for this project was part of the overall project plan entitled "EE/CA and RI/FS Support Sampling Plan, Sauget Area 1" approved by the USEPA on September 9, 1999. BBL's Quality Assurance Manual is provided as Attachment A.

- Documents should be printed, or copied, on both sides of the paper.

  The document will be printed/copied on both sides of the paper, with the exception of some Figures and Tables.

- The document control format should be used in preparing QAPPs. See Element A2.

The document control format will be used for this QA/SAPP. Example as follows:

Sauget Area 1 Site
QA/SAPP
Revision: 0
Date: January 2003
Page: 2 of 10

I TITLE/SIGNATURE PAGE

Signature lines must be included for all project approving officials. See Element A1.

Signature lines have been added for the USEPA, Battelle Marine Sciences, and Brooks Rand, LLC Remedial Project Managers and Quality Assurance Reviewers (Attached).

II 1. Project Organization

A Section 1.1
Provide a Project Organization Chart. See Element A4.

A Project Organization Chart has been provided as Figure 1 (Attached).

B Section 1.1.1 and Section 1.2.4
In Region 5 the Project Manager is usually referred to as the Remedial Project Manager.

Project Managers have been referred to as Remedial Project Managers in the revised QA/SAPP.

C Section 1.1.3
The selected laboratory(ies) must be identified and provide Standard Operating Procedures (SOPs) for all the analytical work being done in this project. The selected laboratory(ies) must also provide SOPs for sample log-in, storage, internal chain of custody, and disposal.

Battelle Marine Sciences Laboratory and Brooks Rand, LLC, have been clearly identified in text and tables as the analytical laboratories and SOPs for all the analytical work, sample log-in, storage, internal chain of custody, and disposal have been included in the QA/SAPP as Attachment B (Attached).

D Section 1.1.4 and Section 1.2.4
In Region 5 the Quality Assurance Manager in Superfund is referred to as the Quality Assurance Reviewer.

Quality Assurance Managers have been referred to as Quality Assurance Reviewers in the revised QA/SAPP.

III 2. Project Background

Provide a copy of the *Sauget Area 1 Dead Creek Sediment Removal Action Mitigation Plan (SRAMP)* (Solutia 2002).

A copy of the Sauget Area 1 Dead Creek Sediment Removal Action Mitigation Plan (SRAMP) (Solutia 2002) will be made available to the Field Services Section by the Remedial Project Manager.

IV 3. Project Description

A Section 3
Provide diagram of the project schedule. See Element A6.

A diagram of the project schedule has been provided as Figure 3 (Attached).

B Section 3.2
Figure 4-1 was not included. Please provide.

The correct figure reference is to Figure 2, the site map, which has been provided in the QA/SAPP. The text has been revised as follows:

> Once located, a sample will be collected from the center of each grid cell at a depth of 0 to 6 inches below ground surface to characterize the biologically active zone, for a total of 60 surface sediment samples (Figure 2).

C Section 3.3 2nd bullet
Nitric Acid is not recommended for decontamination, because Nitric Acid is toxic and may elevate metals concentration.

Nitric acid is recommended in several USEPA and ASTM documents (USEPA, 1994; USEPA, 2000; USEPA, 2002; ASTM, 1990) specifically for decontamination of sampling equipment used to collect samples for metals analysis. No changes have been made to the text. The references below have been cited in the revised QA/SAPP.

> ASTM. 1990. D 5066-90. *Standard Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites*. West Conshohocken, PA.
>
> USEPA. 1994. *Sampling Equipment Decontamination*. Environmental Response Team SOP #2006, Revision 0.0. Edison, NJ.
>
> USEPA. 2002. *RCRA Waste Sampling Draft Technical Guidance - Planning, Implementation and Assessment* (August 2002). Office of Solid Waste and Emergency Response. EPA530-D-02-002.
>
> USEPA. 2001. *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual.* Office of Water. EPA-823-B-021-002.

V 4. Quality Objectives and Criteria for Measurement Data

A Section 4
Data Quality Objective (DQO) levels are not used for Superfund projects in Region 5. EPA requires the use of a systematic planning process. See Element A7. The 7 step DQO process should be itemized and used for all environmental data collection activities. Specify any project action limits that must be met. See documents *Guidance for the Data Quality Objective Process (QA/G-4 or G-4HW)*. Documents are available at the EPA Quality System website.

Text has been added that itemizes the DQO process per appropriate guidance as used in this QA/SAPP (Attached).

B Section 4.1, page 4-3, typo
Reference to Table 23, should be Table 2.

Corrected.

C Section 4.2 and Table 2
The project should indicate any quality control limits for Field Duplicates.

A column for quality control limits for field duplicates has been added to Table 2 (Attached). The text has been revised as follows:

> Quality control limits for field duplicates are also listed in Table 2. Although these quality control limits are only guidelines, frequent failure to meet these limits warrants investigation of the laboratory.

VI 6. Documents and Records

A Section 6.2.1 and elsewhere throughout the QA/SAPP
For Mercury analysis additional sample volume for Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis is not usually collected. For Methyl Mercury analysis the Method 1630 recommends an additional sample for the MS/MSD analysis.

Additional volume for MS/MSDS analysis will be collected for both total and methyl mercury to maintain consistency of sample collection methods. Text has not been modified.

B Section 6.3
Provide copies of the chain-of-custody, sample labels, and custody seals. See Element B3.

Copies of the chain-of-custody, sample labels, and custody seals have been provided in Attachment B of the QA/SAPP (Attached).

C Section 6.5.2
The CLP protocols are not being used. Please itemize the data reporting requirements from the laboratory.

CLP protocols are not being used, as noted in the text. An itemized list of data reporting requirements from the laboratory has been provided in this section, as follows:

In addition to those items mentioned previously, the laboratories are required to report the following:

- Sample analysis summary data sheets;
- Initial and continuing calibration summary sheets;
- Detection limit standard recovery summary;
- Preparation and calibration blank summary;
- Matrix spike and matrix spike duplicate summary;
- Laboratory control sample recovery summary;
- Instrument detection limits;
- Preparation logs;
- Analysis logs; and
- All raw data associated with the analyses.

VII 8. Sampling Method Requirements

Section 8.1.1, typos
The reference to Section 8.2.3, should be Section 8.1.3.

Reference corrected.

The reference to Section 9.4, should be Section 9.3.

Reference corrected.

VIII 10. Analytical Method Requirements

A Section 10.1
Please specify why field data will be *corrected* (collected) for pH, temperature and conductivity. Are water samples being collected and analyzed for Total Mercury and Methyl Mercury? Identify other field measurements that may be made and equipment used. Sediment samples are being collected when no surface water is present according to Section 3.

Because aqueous samples are not being collected for mercury analysis as part of this sampling program, references to additional water quality measurements have been removed from the QA/SAPP, per conversation with Mr. Byvik on 1/22/03.

B Section 10.2.1
The selected laboratory must provide SOPs for Total Mercury and Methyl Mercury analysis. The referenced **USEPA Method 1630** applies for aqueous samples. In addition to the lab SOP for Methyl Mercury analysis, the lab must provide the distillation procedure for sediment samples, and method performance data demonstrating the method generates data of sufficient

precision and accuracy. Copies of SW-846 Method 7471 and USEPA Method 1630 are unacceptable.

Laboratory SOPs for these methods are provided in Attachment B (Attached). Distillation procedures and method performance data have also been included in Attachment B. No method is available for analyzing methyl mercury in a sediment matrix, thus USEPA Method 1630 is modified for this matrix. All references to USEPA Method 1630 have been changed to read "Method 1630 (modified for sediment matrix)."

IX 11. Quality Control Requirements

A Section 11.1.5, editorial
Section 11.5 should be referenced.

Reference to Section 11.5 has been added to section. The text has been revised as follows:

> Further discussion of accuracy checks is provided in Section 11.5.

B Section 11.2.2
Verify if this section is consistent with Section 9.1.

The language in both sections describing the sampling containers has been made consistent. The text has been revised as follows:

> The analytical laboratory will supply appropriate sample containers and preservatives, as necessary. The bottles will be purchased pre-cleaned according to USEPA Office of Solid Waste and Emergency Response (OSWER) Directive 9240.05A requirements.

C Section 11.3.3 and Table 1
For Methyl Mercury analysis the Method 1630 recommends 2 MS/MSDs per batch of 20 samples.

Section 11.3.3 and Table 1 (Attached) have been changed to reflect the recommended number of MS/MSDs per batch of 20 samples. The text has been revised as follows:

> Matrix spike duplicate pairs will be analyzed at a 10 percent frequency (every 10 samples or once every week, whichever comes first).

X 12. Instrument/Equipment Testing, Inspection and Maintenance Requirements

A Table(s) of Preventative Maintenance procedures for Instruments should be included.

Tables of Preventive Maintenance procedures have been provided by each analytical laboratory in Attachment B (Attached).

B Section 12.2
This section could be eliminated if field measurements will not be taken.

Section eliminated per conference call with Mr. Byvik on 1/22/03.

XI 13. Instrument Calibration and Frequency

A Section 13.1
This section could be eliminated if field measurements will not be taken.

Section eliminated per conference call with Mr. Byvik on 1/22/03.

B Section 13.2
The Method 7471 specifies 5 standards and a blank.

Text has been changed to indicate that five standards and a blank will be used, as follows:

> Atomic absorption instruments are calibrated using a minimum of five standards and a blank.

XII 16. Data Management

A Section 16.2.1
Specify field measurements that may be collected, other than measurements for water samples.

All references to additional field measurements (e.g., water quality) have been removed from the QA/SAPP per conference call with Mr. Byvik on 1/22/03.

B Section 16.3, typo
The reference to Section 9.3.3, should be Section 9.2.3.

Corrected.

C Section 16.4.5, typo
The reference to Table 15, should be Table 5.

Corrected.

XIII 17. Assessment and Response Actions

A Sections 17.2 and 17.3
Include provisions that the USEPA may conduct Field and Laboratory Audits.

Text has been added to indicate that USEPA may conduct Field and Laboratory Audits. The text has been revised as follows:

Section 17.2: USEPA may also conduct Field Audits in keeping with customary logistic arrangements with Solutia, Inc.

Section 17.3: USEPA may also conduct Laboratory Audits in keeping with customary logistic arrangements with the laboratory and Solutia, Inc.

B Section 17.4.2
The corrective action should also include re-sampling.

Text has been added to reflect re-sampling as a corrective action. The text has been revised as follows:

The corrective action may include sample re-extraction, re-preparation, re-analysis, cleanup, dilutions, matrix modifications, re-sampling, or other activities.

XIV 18. Reports to Management

Indicate the frequency and recipients of the QA Reports.

A minimum of three QA reports will be generated, one from each analytical laboratory that will accompany the data package, and one from BBL as part of the final deliverable. Additional QA reports may be generated if a significant QA/QC deviation occurs. The text has been revised as follows:

QA reports will be generated by each analytical laboratory and submitted to BBL with the final data package. BBL will include QA statements in its report to Solutia, Inc., as well as in the final report submitted to the USEPA.

XV 19. Data Review, Validation and Verification

Section 19.3.2
The Laboratory QAM should be reviewing all of the data, not just 5 percent, and must be independent of the entity producing the data.

The Laboratory QAM will be reviewing all of the data and the text has been changed accordingly. The text has been revised as follows:

The QAM will review all of the final data reports, and the laboratory director will review a cross section of the final data reports.

XVI 20. Validation and Verification Methods

Section 20.1
The USEPA's Functional Guidelines (USEPA, 1999, and 2002) are only applicable to the CLP SOWs. Data Validation SOPs will have to be prepared for reviewing SW-846 Method 7471 and USEPA Method 1630 data.

Per conference call with Mr. Byvik on 1/22/03, Data Validation SOPs will be prepared and presented at a later date to the USEPA.

XVII Tables

A Table 3, typo
Amend typo in Sediment Reporting Limit column for Methyl Mercury.

Table 3 has been corrected (Attached).

B Table 4
The USEPA Method 1630 specifies Teflon or Borosilicate glass containers for Methyl Mercury.

Table 4 has been changed to reflect borosilicate glass containers for sample containers (Attached).

XVIII Appendices

A Appendix A, Section III, Item 22
Describe in more detail sample collection procedures for Methyl Mercury. Samples for Methyl Mercury should be collected in containers without headspace. These samples should not be homogenized prior to collection due to probable loss of Methyl Mercury.

Text changed to indicate no headspace in sampling containers and text referring to homogenization of samples removed from document. The text has been revised as follows:

> Samples to be analyzed for methyl mercury will be placed in sampling containers with minimized headspace.

B Appendix C, items I and II
Nitric Acid is not recommended. Nitric Acid is toxic and may elevate metals concentration.

Nitric acid is recommended in several USEPA and ASTM documents (USEPA, 1994; USEPA, 2000; USEPA, 2002; ASTM, 1990) specifically for decontamination of sampling equipment used to collect samples for metals analysis. No changes have been made to the text. The references below have been cited in the QA/SAPP.

ASTM. 1990. D 5066-90. *Standard Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites*. West Conshohocken, PA.

USEPA. 1994. *Sampling Equipment Decontamination.* Environmental Response Team SOP #2006, Revision 0.0. Edison, NJ.

USEPA. 2002. *RCRA Waste Sampling Draft Technical Guidance - Planning, Implementation and Assessment* (August 2002). Office of Solid Waste and Emergency Response. EPA530-D-02-002.

USEPA. 2001. *Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual.* Office of Water. EPA-823-B-021-002.

C Appendix D

These Field Instruments may not be used in collecting sediment samples. However, the SOP should include sensitivity, precision and accuracy criteria, frequency for calibration/recalibration and duplicate measurements, and quality control acceptance criteria. See Sections 10.1 and 11.2.1, also.

This appendix has been deleted. Aqueous sampling is not being conducted under this QA/SAPP (per conversation with Mr. Byvik on 1/22/03).

Attachment A to the QA/SAPP

BBL Quality Assurance Manual

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Quality Assurance Manual

Table of Contents

Page No.

1 Introduction

Blasland, Bouck & Lee, Inc. (BBL) and its affiliated companies (the Firm) have developed a Quality Assurance Program to meet the quality needs of our clients by establishing a system through which critical-to-quality characteristics are defined, and appropriate quality procedures are implemented. The Firm is committed to consistently providing deliverables that meet client and regulatory requirements, and addressing client satisfaction through the effective application of the Quality Management System. This includes processes for continual improvement and the prevention of nonconformity.

Collectively, the information and policies identified in this document shall be referred to as the Quality Manual. The purpose of this manual is to identify the scope of the Quality Management System, identify documented procedures, and describe the sequence and interaction of the processes included in the Quality Management System. Process requirements and guidance of the Firm's quality system are presented in the Quality Assurance Procedures. Project-specific plans are prepared to provide guidance to meet project-specific quality needs.

2 Scope

This Quality Manual applies to the full range of activities performed by the Firm, whose employees are committed to providing quality services and deliverables to clients. Many of the Firm's activities are based upon project management elements involving collecting and evaluating data; designing, constructing, and operating systems; and providing management consulting services. These and all other activities affecting quality must consistently meet the intended use, purpose or scope of work, meet or exceed client expectations, comply with regulatory requirements, and meet cost considerations.

Permissible exclusions allow the Firm to identify and exclude Quality Management System requirements that do not affect the organization's ability to provide deliverables that meet client and applicable regulatory requirements. These exclusions will be documented and are limited to requirements from section 7 of the Quality Manual, and may be due to the nature of the Firm's products, client requirements, and applicable regulatory requirements.

3 Quality Policy

3.1 Mission Statement

We will always provide our clients with unparalleled service. We view our relationship with our clients as a long-term partnership founded upon superior service, technical excellence, breakthrough thinking, and an in-depth knowledge of their businesses.

BBL is committed to treating each and every one of our clients as the most important client we have, and to meeting their needs in a way that best utilizes their vital resources. We will work as a coordinated team of professionals and focus the finest talent available on each opportunity. We pledge to continually explore ways to enhance the value of our services.

3.2 Quality Principles

The BBL Quality Management System is summarized by twelve Quality Principles, which form the basis for all quality assurance activities:

• Quality is the responsibility of all employees, who must strive for continuous improvement, building quality into every activity to produce the unparalleled services our clients expect.

• All work activities must be planned based on the client's needs, taking into account quality goals, and applicable technology and regulatory requirements.

• Personnel must be qualified to implement the work activities to which they are assigned. Objective evidence of qualifications must be established and maintained.

• Procedures must be developed, documented, and approved for project activities. All such work must be performed and documented in accordance with the approved procedures.

• Activities involving the acquisition of data must be planned and documented in order to identify the type, quality and quantity of data needed for the intended use.

• The procurement and use of materials, equipment, and services that affect the quality of the Firm's work must be planned and managed, and must conform to applicable contract, technical, and regulatory requirements.

• All designs, plans, specifications, and other documents must be developed using sound engineering and scientific principles, and must meet appropriate industry standards. All designs, plans, specifications, and other documents must be reviewed, verified, and approved prior to issuance.

• Complete, accurate, and up-to-date records must be prepared and maintained for all project and program activities.

• Sampling, measuring, and testing equipment must be maintained and calibrated in accordance with manufacturer's recommendations and industry standards. Calibration and maintenance records must be maintained.

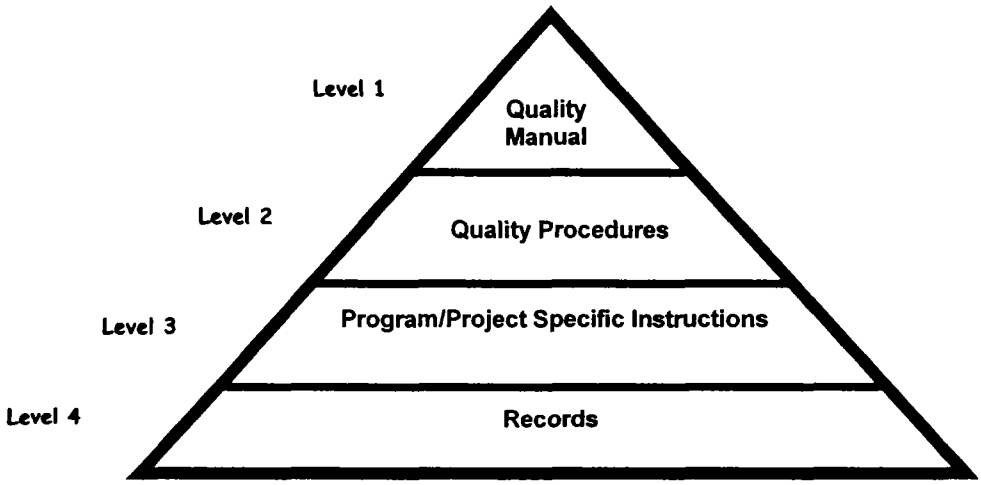
• Computer software and computer hardware/software configurations used in engineering, scientific, and accounting programs must be managed, maintained, and documented.

• Deviations from planned project activities must be documented and reported to management as they occur. The significance of a deviation on the project must be determined and appropriate adjustments must be made.

• Engineering, scientific, and construction activities will be periodically evaluated to verify conformance with quality, technical, and regulatory requirements.

4 Quality Management System

The Firm's Quality Management System is a guiding process based on meeting or exceeding client requirements. *Planning* activities are designed to identify the processes needed, and to determine the sequence and interaction of these processes. *Implementation* methods provide effective control of these processes, and the availability of information necessary to support the work activities. *Review* methods are in place to measure, monitor and analyze these processes. *Improvement* activities implement action necessary to achieve planned results and sustain continual improvement.



Our Quality Management System Model is defined in four levels of documentation:

Level 1	BBL Quality Manual	Directive Policies
Level 2	Quality Procedures / Major Processes	What and Who
Level 3	Project-Specific Work Instructions	How
Level 4	Quality-related Records	What was done

The figure above illustrates the Quality Management System for all activities and services provided to our clients. The Quality Manual provides a core set of policies for use across the Firm's entire client base. The Quality Management System also recognizes the fundamental differences between the various services that the Firm provides to our clients, thus allowing for program/project activities (procedures and work instructions) which are applicable to specific clients.

Quality is an integral part of the work conducted by the Firm. The Quality Management System is designed to address managerial aspects common to the success of projects, and has been established and integrated into the Firm's work activities. Selecting appropriate quality requirements is a management function such that the results are of the type and quality needed and expected by the client.

The Quality Management System is reviewed and updated to reflect physical changes in the organization as well as changes in policy. This review is performed annually or more frequently, as deemed necessary by management.

5 Management Responsibility

5.1 Management Commitment

Evidence of management's commitment to the development and improvement of the Quality Management System is shown by communicating the importance of meeting client, regulatory, and legal requirements to the organization. The quality policy and quality objectives are established, management reviews are conducted, and necessary resources are provided.

It is management's responsibility to maintain an atmosphere in which all employees strive for quality and continuous improvement. Management at the corporate, division, and project level must lead the implementation of the Quality Management System. Quality is the responsibility of all employees, who must work as a team, building quality into every project to produce the unparalleled services our clients expect.

The Firm will provide adequate measures to verify that the Quality Management System is understood and implemented. The Firm will also provide adequate resources and delegate authority and independence to management and staff, enabling them to effectively plan, implement, assess, and improve the organization's quality system.

The assessment process will evaluate the establishment, documentation, and effective implementation of the quality system. Management will regularly assess the adequacy of the system, identify appropriate actions resulting from these assessments, and verify that corrective actions are completed in a timely manner. Factors that hinder the organization from meeting quality objectives are identified and corrected.

5.2 Quality Policy

The quality policy declares the purpose of the Firm's QMS. It includes a commitment to meeting requirements and to continual improvement, the establishment and review of quality objectives, and the communication and organizational understanding of the policy. Additional declarations include the review for continuing suitability, the determination of client needs and expectations, the conversion of these needs into requirements, and fulfilling these needs with the aim of achieving client satisfaction.

5.3 Quality Planning

Effective planning includes the identification of measurable quality objectives needed to meet client requirements that are established at relevant functions and levels within the organization. Resources needed to achieve the quality objectives are identified and planned. The output of this planning is documented in Quality Plans (refer to section 7 of this manual) which include the identification of relevant processes and procedures, consideration of permissible exclusions, resource needs, control of project and scope changes, and continual quality improvement.

5.4 Responsibility, Authority and Communication

Organizational functions and their interrelations within the Firm, including responsibilities and authorities, are defined and communicated to facilitate effective quality management. The various levels of the Firm communicate the processes of the Quality Management System and their effectiveness.

5.5 Management Representatives

The Quality Officer(QO) and Quality Manager(QM) have the responsibility to verify that processes of the Quality Management System are established and maintained. The QO and QM report to senior management on the performance of the quality system and the needs for improvement. The QO, QM, and senior management are responsible for promoting awareness of client requirements throughout the organization.

5.6 Quality Management System Documentation Control

Quality System documents include the Quality Manual, the Quality Policy, procedures, and forms. These are approved and updated, as necessary, prior to issuance. Current revision status of documents is identified, relevant versions of applicable documents are available at points of use, and all documentation will remain legible, readily identifiable, and retrievable. Measures are in place to prevent the unintended use of obsolete documents and to apply suitable identification to them if they are retained for any purpose. Documents of external origin are identified and their distribution is controlled.

5.7 Control of Quality Records

Records required for the Quality Management System are maintained in order to provide evidence of conformance to requirements, and evidence of effective operation of the Quality Management System. A procedure exists for the identification, storage, retrieval, protection, retention time, and disposition of quality records.

5.8 Management Review

Top management reviews the inputs and outputs of the Quality Management System at planned intervals to verify its continuing suitability, adequacy, and effectiveness. The review evaluates the need for changes to the organization's Quality Management System, including the quality policy, quality objectives, and procedures. These reviews are recorded.

Inputs to management review include performance-improvement opportunities related to the results of audits, client feedback, process performance and product conformance, status of preventive and corrective actions, follow-up actions from earlier management reviews, and changes that could effect the Quality Management System.

The outputs from the management review include actions related to improvements of the Quality Management System and its processes, improvement of product related to client requirements, and resource needs.

6 Resource Management

The Firm determines and provides, in a timely manner, the resources needed to implement and improve processes of the Quality Management System.

6.1 Human Resources

Personnel who are assigned responsibilities defined in the Quality Management System are competent on the basis of applicable education, training, skills, professional licensing, and experience. Competency needs for personnel performing activities affecting quality are identified, training is provided to satisfy these needs, and the effectiveness of the training provided is evaluated. Employees are aware of the relevance and importance of their activities and how they contribute to the achievement of the quality objectives. Education, experience, training, licensing, and qualification records are appropriately maintained.

6.2 Facilities

The human and physical factors of the work environment, including workspace, associated facilities, equipment, hardware, software, and supporting services are identified, provided, and maintained for achieving conformity of deliverables and services.

7 Activities for Providing Deliverables

This section applies to the sequence of processes and sub-processes required for providing deliverables and/or services meeting or exceeding client expectations.

7.1 Quality Planning

Planning activities begin with the identification of client requirements and the establishment of quality objectives for these requirements. Additional activities include the identification of current applicable procedures, and the need to establish processes, documentation, and provide resources and facilities specific to client requirements. The Firm will establish criteria for the performance of verification and validation activities. Records necessary to provide objective documentation of conformity of the processes and resulting work-product will be identified and retained.

7.2 Client Requirements

During the identification of client requirements, considerations are given for requirements specified by the client, including the requirements for availability, delivery and support, requirements not specified by the client but necessary for intended or specified use, and regulatory and legal requirements. A review of these requirements is conducted prior to committing the Firm to supply deliverables to the client (e.g., submission of a tender, acceptance of a contract or order). Client requirements are defined, confirmed before acceptance, contract or order requirements differing from those previously expressed (e.g. in a tender or quotation) are resolved, and the Firm's ability to meet defined requirements is verified. Review and follow-up actions will be recorded.

7.3 Control of Changes

When requirements are changed, relevant documentation is amended and affected personnel are made aware.

7.4 Client Communication

Avenues are in place for communicating information, inquiries, contracts, order handling, amendments, client feedback, and client complaints.

7.5 Project Management Activities

The Project Management Handbook provides essential tools for successful planning and implementation of projects.

7.5.1 Planning

Planning identifies the processes needed to meet or exceed client requirements, review, verification, and validation activities appropriate to each design and/or development stage, and the responsibilities and authorities for these activities. Interaction between different groups involved in design and/or development is managed for effective communication and understanding of responsibilities. Planning output is updated as activities progress.

7.5.2 Inputs (Deliverable Requirements)

Requirements are defined and documented. These are reviewed for adequacy so that incomplete, ambiguous or conflicting requirements are resolved. Examples include:

a) functional and performance requirements;
b) applicable regulatory and legal requirements;
c) applicable information derived from previous similar designs; and
d) other requirements deemed essential.

7.5.3 Outputs

Outputs are documented to enable verification against design and/or development inputs to meet the input requirements, provide appropriate information for production and service operations, contain or reference acceptance criteria, and define the characteristics of the deliverable that are essential to its safe and proper use. Output documents are approved prior to release. Examples of outputs include:

a) drawings
b) proposals
c) QAPPs and HASPs
d) reports
e) project plans

7.5.4 Review

Reviews of design and/or development are conducted to evaluate the ability to fulfill requirements and to identify problems and propose follow-up actions. Reviews include representatives of functions concerned with the design and/or development stage(s) being reviewed. Results of reviews and subsequent follow-up actions are recorded.

7.5.5 Verification

Action is taken to verify that the outputs meet the design and/or development inputs. Results of verification and subsequent follow-up actions are recorded.

7.5.6 Validation

Validation confirms that the resulting deliverable is capable of meeting its intended use. When applicable, validation is completed prior to the delivery or implementation of the deliverable. When impractical, partial validation is performed to the extent applicable. Results and subsequent follow-up actions are recorded.

7.5.7 Control of Changes

Changes are identified, documented, and controlled, including evaluation of the effect of the changes on deliverables. The changes will be verified and validated, as appropriate, and approved before implementation. Results of the review of changes and subsequent follow-up actions are documented.

7.6 Purchasing

7.6.1 Purchasing Control

Purchased products and services are verified for conformance to requirements. The type and extent of control is dependent upon the effect that purchased items have on the Firm's processes and deliverables. Suppliers are evaluated and selected based on their ability to supply product and services in accordance with the Firm's requirements. Selection criteria and periodic evaluations are defined. Results of evaluations and follow-up actions are recorded.

7.6.2 Purchasing Information

Purchasing documents contain information describing the product or service to be purchased, including, where appropriate, requirements for approval or qualification of product, procedures, equipment and personnel, and the Quality Management System. The adequacy of specified requirements presented in the purchasing documents will be verified prior to their release.

7.6.3 Verification of Purchased Product

Activities necessary for verification of purchased product are identified and implemented.

7.7 Deliverables and Services Activities

7.7.1 Deliverables and Services

Deliverables and service activities are controlled through information that specifies the characteristics of the deliverable, and the availability of work instructions, where necessary. Control is also achieved through the use and maintenance of suitable equipment used during operations, the availability and use of measuring and monitoring devices, the implementation of monitoring activities, and the implementation of defined processes for release, delivery, and post-delivery activities.

7.7.2 Identification and Traceability

Where appropriate, identification is established for work-product throughout deliverable and service activities. Where traceability is a requirement, unique identification is controlled and recorded. Status of the deliverable is identified with respect to review and approval activities.

7.7.3 Client Property

Care with client property is exercised while such property is in the Firm's control or use, by identifying, verifying, protecting, and maintaining the client property provided for use or incorporation into the deliverable. This may include intellectual property (e.g. information provided in confidence). Incidents in which client property is lost, damaged or otherwise found to be unsuitable for use are recorded and reported to the client.

7.7.4 Preservation of Deliverables

The Firm preserves conformity of the deliverable with client requirements during internal processing and delivery to the intended destination. This includes identification, handling, packaging, storage, and protection.

7.7.5 Validation of Processes

Validation of production and service processes demonstrates the ability of the processes to achieve planned results where the resulting output cannot be verified by subsequent measurement or monitoring. This includes any processes where deficiencies may become apparent only after the deliverable is in use or the service has been delivered. Applicable validation includes qualification of processes, equipment and personnel, use of defined methodologies and procedures, requirements for records, and re-validation.

7.8 Control of Measuring and Monitoring Devices

Measurements and the measuring and monitoring devices required for assuring conformity to specified requirements are identified. Measuring and monitoring devices are used and controlled to verify that measurement capability is consistent with the measurement requirements.

Where applicable, measuring and monitoring devices are calibrated and adjusted periodically or prior to use against devices traceable to international or national standards. Where no such standards exist, the basis used for calibration is recorded, safeguarded from adjustments that would invalidate the calibration, and protected from damage and deterioration during handling, maintenance and storage. Calibration results are recorded, the validity of previous results are re-assessed if found to be out of calibration, and corrective action is taken. Software used for measuring and monitoring of specified requirements is validated prior to use.

8 Measurement Analysis and Improvement

8.1 Planning

Measurement and review activities necessary to assure conformity and achieve improvement are defined, planned and implemented. This includes the determination of the need for, and use of, applicable methodologies and statistical techniques.

8.2 Measuring and Review

8.2.1 Client Satisfaction

Information regarding client satisfaction is solicited, reviewed, measured, and addressed.

8.2.2 Internal Audits

Internal audits are used to verify that the Quality Management System conforms to the requirements of the ISO 9000:2000 International Standard, and that the system has been effectively implemented and maintained. The audit program takes into consideration the status and importance of the activities and areas to be audited as well as the results of previous audits. The audit scope, frequency, and methodologies are defined, and audits are conducted by personnel other than those who perform the activity being audited.

Responsibilities and requirements are defined for conducting audits, ensuring their independence, recording results, and reporting to management. Management takes timely corrective action to address deficiencies found during audits. Follow-up actions verify the implementation of corrective action and the reporting of verification results.

8.2.3 Processes

Suitable methods are applied for measurement and review of those processes necessary to meet client requirements. These methods confirm the continuing ability of each process to satisfy its intended purpose.

8.2.4 Deliverables

Characteristics are measured and reviewed to verify that requirements are met and carried out at appropriate stages. Evidence of conformity with the acceptance criteria is documented, and records indicate the authority responsible for release of deliverables. Deliverables and/or services will not be released until all the specified activities have been satisfactorily completed, unless otherwise approved by the client.

8.3 Control of Nonconformity

Deliverables that do not conform to requirements are identified and controlled to prevent unintended use or delivery. These activities are defined in a documented procedure. Nonconformances are corrected and subject to re-verification, demonstrating conformity. When nonconforming deliverables are detected after delivery or use has started, appropriate action is taken based on the consequences of the nonconformity. Proposed rectification of the nonconformance is reported to the client, the end-user, regulatory body, or other interested party, as appropriate.

8.4 Analysis of Data

Data are collected and analyzed to determine the suitability and effectiveness of the Quality Management System, and to identify improvements. Data are analyzed to provide information on client satisfaction, conformance to client requirements, characteristics of processes, deliverables and their trends, and suppliers.

8.5 Continual Improvement

8.5.1 Planning

Processes necessary for the continual improvement of the Quality Management System are planned and managed. Continual improvement is facilitated through the use of the quality policy, objectives, audit results, analysis of data, corrective and preventive action, employee input, and management review.

8.5.1 Corrective Action

Corrective action is taken to eliminate the cause of nonconformities in order to prevent recurrence; the action taken is appropriate to the impact of the problems encountered. A procedure exists for identifying nonconformities (including client complaints), determining the causes of nonconformity, evaluating the need for actions to verify that nonconformities do not recur, determining and implementing the corrective action needed, recording results of action taken, and the review of corrective action taken.

8.5.2 Preventive Action

Preventive action is taken to eliminate the causes of potential nonconformities in order to prevent occurrence; actions taken are appropriate to the impact of the potential problems. A procedure exists for identifying potential nonconformities and their causes, determining and implementing the preventive action needed, recording results of action taken, and the review of preventive action taken.

Revision to the QA/SAPP

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Revision to the QA/SAPP

Figure 1

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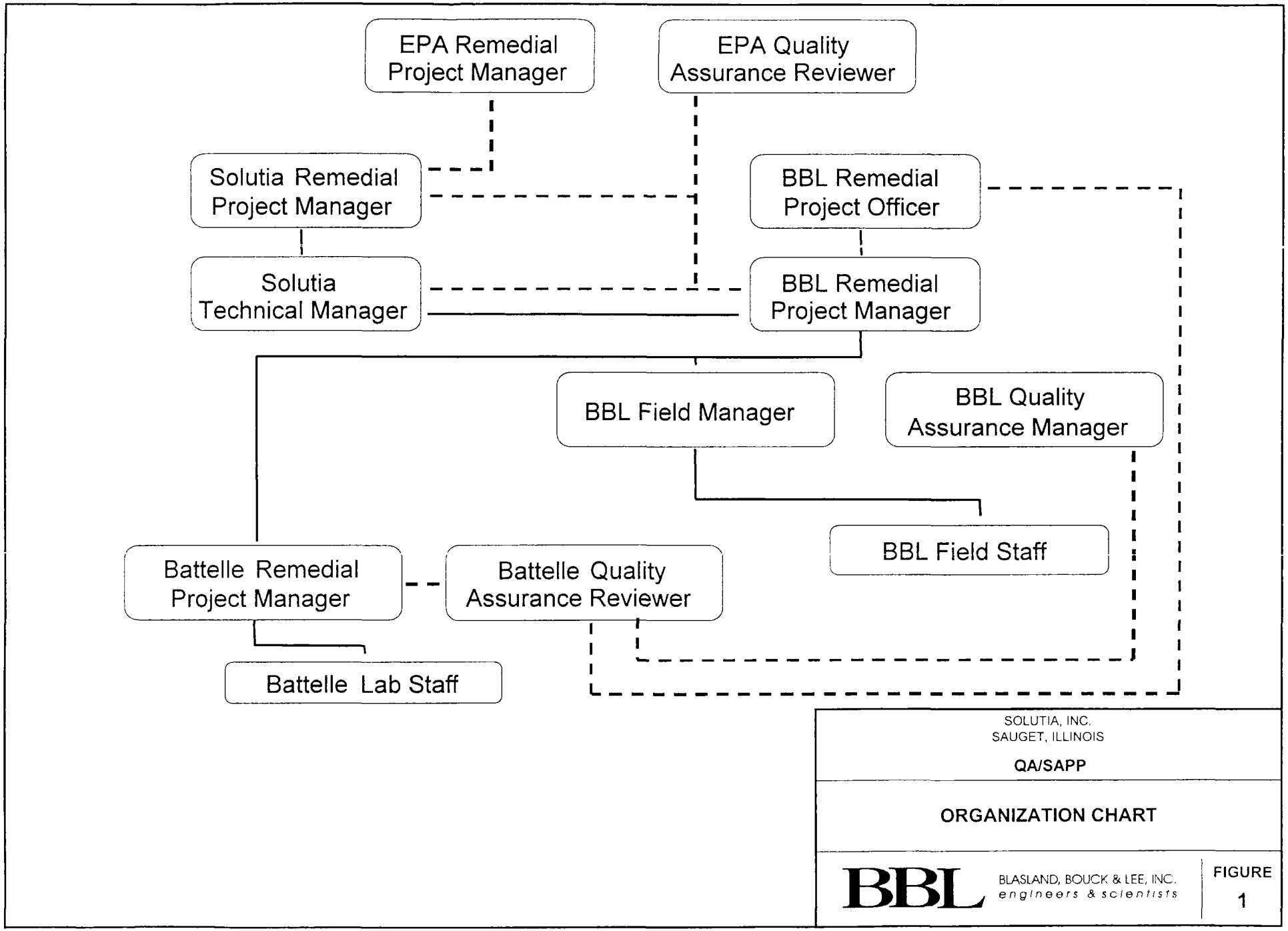

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QA/SAPP

ORGANIZATION CHART

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FIGURE 1

mis_Figure 1 xls_Figure 1_1-30-2003

Attachment B to the QA/SAPP

Laboratory Quality Assurance Manuals

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SOP #BR-0011

Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630 (Draft, 1/01)

Brooks Rand, LLC

Revision 007
Revised 10/14/02
Written 1/90

Reviewed _____

CONFIDENTIAL

_____ President	11/11/02 Date
_____ QA Manager	10/18/02 Date
_____ Senior Scientist	10/18/02 Date
_____ Scientist (if applicable)	_____ Date

Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630 (Draft, 1/01)

1. SCOPE AND APPLICATION

1.1. This method is for the determination of methyl mercury in waters, sediments, and biota by either distillation or extraction, aqueous phase ethylation, purge and trap, isothermal GC separation, and cold vapor atomic fluorescence spectrometry.

2. SUMMARY OF METHOD

2.1. Mono-methylmercury (MMHg) is determined by an improved method (Liang, Bloom, and Horvat 1994). The MMHg is first ethylated with sodium tetraethylborate ($NaBEt_4$) and collected by purging with dry, Hg free Nitrogen onto a quartz tube filled with either Carbotrap™ or Tenax. The ethyl mercury derivatives are then thermally desorbed and transferred to a GC column held in an oven at 105° C, which separate the species by mass chromatographically. The ethylated Hg compounds are decomposed at 900° C to Hg(0), then quantified by a cold vapor atomic fluorescence spectrophotometer (CVAFS). This method can be applied for the determination of MMHg in a variety of sample matrices and has been demonstrated as being very sensitive, precise, and accurate. Very good results were obtained for the determination of MMHg in standard and certified reference materials and numerous intercalibration samples (Liang, Bloom, and Horvat 1994).

3. INTERFERENCES

3.1. If properly applied, the distillation procedure will remove most to all significant interferences. However, the concentration of HCl in the solution will affect the distillation of methyl mercury from the solution. Too little HCl will cause the distillation of methyl mercury to not be quantitative while too much HCl will cause the co-distillation of HCl fumes, which interfere with the ethylation process. EPA Draft Method 1630 dictates that fresh water samples must be preserved with only 0.3% to 0.5% (v/v) 11.6 M HCl and that salt water samples must be preserved with 0.2% to 1.0% (v/v) 9 M H_2SO_4.

3.2. Samples must not be preserved with nitric acid as it may cause partial decomposition of the analyte during distillation.

3.3. Positive artifact is possible with the distillation of samples that are high in inorganic mercury. Ambient organic matter may methylate 0.01% to 0.05% of the ambient inorganic mercury during ethylation. In inorganic mercury contaminated waters this can

significantly affect the results for methyl mercury. Solvent extraction may be preferable to distillation in samples that are high in divalent mercury (Hg(II)).

4. APPARATUS AND MATERIAL

4.1. Atomic fluorescence spectrophotometer (BRL part #AF-03): CVAFS systems are built by Brooks Rand, LLC (BRL Model III). Refer to the "Brooks Rand, LLC Model III Operations Manual" (included with this SOP) for instrument operating instructions.

4.2. Data Acquisition : Integration software (BRL Mercury Guru Version 2.0 or later) with PC for peak area measurements. Alternatively a chart recorder (Yokogawa 3021) for peak height measurements may be used. The installation and use of the Guru software is described in the "Brooks Rand, LLC Model III Operations Manual."

4.3. Reaction and purge vessels (BRL part #AF-32): A 150 mL flat bottom bottle with 24/40 tapered fitting is used as the reaction vessel, in conjunction with a special 4-way valve sparging-tube cap-assembly. This valve assembly allows the prepared sample to react with the ethylating reagent without bubbling, and then to be purged onto the trapping column. Finally, the valve assembly allows the prepared sample to be bypassed so that water vapor adsorbed onto the column may be evaporated by the direct flow of dry carrier gas.

4.4. Trapping column (BRL part #AF-21): Tenax traps used for the collection of purged organomercury species measuring 10 cm long of 6.4 mm outside diameter x 4.0 mm inside diameter. Figure 1 also shows the connection of the column and a reaction vessel.

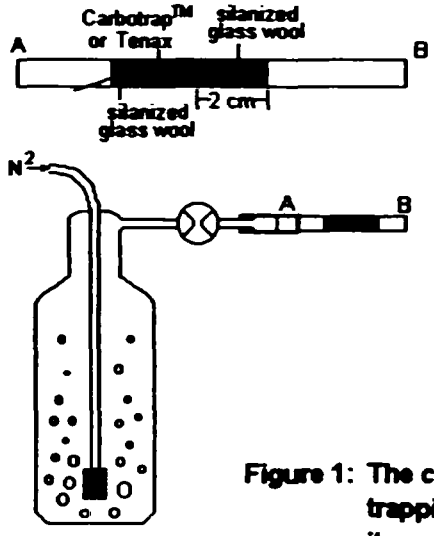

Figure 1: The construction of trapping column and its connection with a reaction vessel

4.5. Guard Column: If a Tenax TA trap is to be used for collecting purged species, a pre-GC column OV-3 trap must also be used. This guard column is placed between the Tenax trap and the GC column and serves to inhibit Tenax material from entering the GC

column. The guard column consists of approximately 70 mg of OV-3 3% packed in the same type of quartz tube used for the trapping column, between quartz wool plugs. The guard column is initially conditioned by heating twice for 30 seconds, allowing the trap to cool between heatings. The guard column should be blanked daily with the trapping columns before analysis. Guard columns should be replaced routinely at least every four (4) months or when a problem arises.

4.6. Isothermal gas chromatography system: consisting of GC column (BRL part #AF-34), GC oven (BRL part #AF-33), pyrolitic column (AF-35) and temperature controller for GC oven (BRL part #AF-36). For a diagram of the system see Figure 2. Under a 30 mL/min flow of high purity helium, organomercury species desorbed from a trapping column are carried by gas passing through the GC column, held at 105° C in a cylindrical oven, and eluted. Separated species are decomposed in a thermal decomposition tube and finally detected by CVAFS.

5. REAGENTS, GASES, AND WATER

5.1. MMHg Standard solutions

a) Standard stock solution: 1 mg/mL MMHg is purchased from a known, accredited vendor.

b) Intermediate stock solution: 1 µg/mL MMHg. Dilute 0.10 mL of 1 mg/mL stock solution to 100 mL with DDW. This solution expires after one month.

c) Working standard: 1 ng/mL MMHg. Dilute 0.10 mL of 1 µg/mL intermediate stock solution to 100 mL with DDW. This solution expires daily.

5.2. Sodium tetraethylborate ($NaBEt_4$) solution: Dissolve 1.0 g of $NaBEt_4$ (stored in freezer) in 100 mL of 2.0% KOH solution that has been chilled to 0° C to produce a 1.0% working solution. This solution is decanted into individual 5.0 mL Fluoropolymer vials. This reagent is stored at < -10° C and is defrosted prior to use. The solution expires daily upon unfreezing. A new batch of the ethylating reagent should be made as soon as there are any doubts about its quality (i.e. low recovery of matrix spikes). $NaBEt_4$ solids and solutions must not be used if they have become yellow.

5.3. Sodium acetate buffer: A 2M acetate buffer is prepared by dissolving 272 g of reagent grade sodium acetate and 118 mL of glacial acetic acid in DDW to a final volume of 1 L. This solution is purified of trace mercury by the addition of 5 g of 1 N HCl-rinsed sulfhydoxyl chelating resin (Sumitomo Q-10R) to the bottle and agitation. The solution is stored in a Fluoropolymer bottle.

5.4. Methanolic potassium hydroxide solution: Dissolve 250 g of reagent grade KOH pellets in high purity methanol to a final volume of 1 L. The solution is stored in a Fluoropolymer bottle.

5.5. Gases: Helium used as a GC carrier gas is ultra high-purity grade. Nitrogen used as a purge gas for sweeping derivatives from a bubbler is plumbed from cryogenic bleed-off. Both are passed through a gold-coated sand trap to remove traces of mercury prior to use.

5.6. Water: Double Deionized Water (DDW) from a Millipore System is used throughout.

5.7. 20 % KCl / 0.2 % L-Cysteine solution: Dissolve 10.0 g KCl and 0.1 g L-Cysteine in 50 mL of DDW. This solution must be discarded and replaced every 6 months or if crystals begin to form.

5.8. 9 M H_2SO_4: Mix equal parts DDW and pre-analyzed, concentrated H_2SO_4. Introduce the reagents slowly as this procedure generates a great deal of heat. Allow to cool completely before capping tightly.

5.9. 0.05 % NH_2OH•HCl: Dilute 400 µL of 30 % NH_2OH•HCl, used for Total Hg analysis, to 240 mL DDW. Discard and replace after one month.

6. SAMPLE COLLECTION, STORAGE, AND HANDLING, AQUEOUS, SEDIMENTS, AND BIOLOGICAL MATERIALS.

6.1. Water

6.1.1. Samples should be collected into only rigorously cleaned Fluoropolymer bottles or glass bottles with Fluoropolymer lined lids. Under no circumstances should ordinary plastic (i.e.; polyethylene, polypropylene, or vinyl) containers be used, as they are very diffusive to gaseous Hg(0) from the air. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Gill and Fitzgerald, 1985). As an added precaution, clean bottles are filled with high purity 0.4% HCl solution and capped, dried, and double-bagged in new zip-loc bags in the clean-room, and stored in wooden or plastic boxes until use.

6.1.2. Samples are collected using rigorous, ultra-clean protocols (Gill and Fitzgerald, 1985; and EPA Method 1669 "Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels", April 1995) which are summarized as follows:

a) At least two persons wearing fresh clean-room gloves at all times, are required on a sampling crew.

b) One person ("dirty hands") pulls a bagged bottle from the box, and opens the outer, dirty bag, avoiding touching inside that bag.

c) The other person ("clean hands") reaches in, opens the inner bag, and pulls out the sample bottle.

d) The bottle is opened with a plastic shrouded dedicated wrench, and the acidified water is neutralized and discarded downstream of the sampling site.

e) The bottle is rinsed once with sample water, and then filled.

f) Preservative (i.e.; 0.4% by volume of high purity 12 M HCl) may be added at this time, or within several hours after receipt at the clean laboratory. Saline samples should be preserved with 0.2% by volume of high purity 9 M H_2SO_4.

g) The cap is replaced with the wrench, and the bottle rebagged in the opposite order from which it was removed.

h) Clean-room gloves are changed between samples and whenever something not known to be clean is touched.

i) Water samples are best obtained by surface grab, using gloved hands, and facing into a flowing body of water (i.e.; looking upstream or of the bow of a moving boat). If samples are to be taken from depth, the only non-contaminating method generally available is pumping. Two methods have been found to work in this regard. The first is to use rigorously acid-cleaned Fluoropolymer tubing, and a peristaltic pump with *freshly cleaned* (heating to 70° C in 5% HCl + CH_3COOH) silicon tubing. Beware that once cleaned, silicon tubing quickly absorbs Hg from the air The other method involves high-volume pumping (i.e.; 50 $L \cdot min^{-1}$) through neoprene hose. If this method is used, it is best to clean the system first by pumping several hundred liters of 5% HCl solution, and then pumping clean water for several hours. This second technique works largely because the rate of flow is so fast that the contamination becomes imperceptibly diluted.

j) DISCRETE SAMPLERS, i.e.; Niskin, GoFlo, and Kemerer BOTTLES, ARE TO BE AVOIDED, AS EVEN UNDER THE BEST OF CONDITIONS THEY ARE OFTEN FOUND TO GROSSLY CONTAMINATE SAMPLES AT THE $ng \cdot L^{-1}$ LEVEL.

6.1.3. Samples are preserved by adding 4 $mL \cdot L^{-1}$ of concentrated HCl (if only total methylmercury is to be analyzed), or frozen if labile and methylmercury are to be analyzed. Saline samples ($[Cl^-]$>500 ppm) are preserved with 2 $mL \cdot L^{-1}$ of 9 M H_2SO_4 solution. Samples may also be sent back to the laboratory unpreserved if they are 1) collected in Fluoropolymer bottles, 2) filled to the top with no head

space, and 3) sent at 0 – 4° C by overnight mail. The samples should be preserved and analyzed soon after collection (within 48 hours). FREEZING IS NOT AN ACCEPTABLE TECHNIQUE FOR TOTAL INORGANIC Hg, AS UPON THAWING, MUCH Hg(II) IS CONVERTED TO VOLATILE Hg^0.

6.1.4. Acid preserved samples are stable for at least six months, if they are kept cool and in the dark.

6.1.5. All handling of the samples in the lab is to occur by clean-room gloved personnel in a class-100 clean room station with mercury removal filters, after rinsing the outside of the bottles in low Hg water, and drying in the clean air hood.

6.2. Solids

6.2.1. Samples should be collected only into rigorously cleaned Fluoropolymer containers or glass containers with Fluoropolymer lined lids. Under no circumstances should polyethylene, polypropylene, or vinyl containers be used.

6.2.2. Samples are to be frozen at <-10°C (standard freezer on coldest setting) until use. A holding time of 1 year at <-10°C is recommended.

6.2.3. All dissection, homogenization, and other handling of the samples is to occur by clean-room gloved personnel in a class-100 clean room station with mercury removal filters.

7. SAMPLE PREPARATION

Depending on the purposes and definitions of investigations of mercury biogeochemistry cycling, samples are prepared in the following methods prior to analysis.

7.1. Preparation of aqueous samples for MMHg analysis.

The following two isolation methods, distillation and solvent extraction, have been used in our labs for the determination of MMHg in aqueous samples. Good agreement was obtained in the comparison of the two methods for most water samples studied: for organic rich and/or high level sulfide containing samples, the distillation showed some advantages over the solvent extraction method with higher recoveries (85 ± 4%, Horvat, Bloom, and Liang, 1993). In addition, extraction consumes large quantities of organic solvent which can result in environmental contamination. Therefore, distillation is preferred.

7.1.1. Distillation:

Reagents: 20% KCl in 0.2 % L-Cysteine, 9 M H_2SO_4, 0.05% $NH_2OH{\cdot}HCl$

Distillation devices: Vials and caps for distillation and distillate collection are made of Fluoropolymer obtained by Savillex Corporation, USA. Caps have 1/8" ports for friction fit 1/8" Fluoropolymer tubing. Instead of Fluoropolymer, a glass distillation still may also be used (Horvat and Stoeppler, 1988).

Distillation procedures: An aliquot of water sample, typically 40 mL, is transferred into a 60 mL Fluoropolymer vial (for high MMHg concentration samples, small sample size should be used, but bring the final volume to a known volume with DDW). Add 0.2 mL of the 20% KCl/0.2 % L-Cysteine solution and 0.5 mL of 9 M H_2SO_4. Start the distillation immediately after addition of reagents at a nitrogen flow rate of approximately 73 $mL \cdot min^{-1}$ (rotometer set at 10) and at a heating block temperature of 145° C. Note: The liquid nitrogen tank must be at least $1/8^{th}$ full prior to beginning any distillation. This is judged by the gauge on top of the tank and not by the tank pressure. The distillate is collected in a 60 mL Fluoropolymer vial containing 5 mL of 0.05% $NH_2OH \cdot HCl$ in DDW, which is cooled in an ice-water bath. The distillation is finished when the final distillate volume is 45 mL, as measured against a reference vial. This typically takes from 2 to 3 hours. Bring the final volume of the receiving vial to the 58 mL mark with DDW. Depending on its MMHg concentration, transfer an aliquot of the distillate into the methylation reaction vessel for analysis as described in section 4. Note: Open the flow of nitrogen for up to one hour before beginning the distillation to purge the lines of room air and other possible contaminants.

7.1.2. Solvent extraction

Reagent: 30% KCl (saturated), methylene chloride (large blanks in MMHg determination occasionally result from this solvent. Therefore, different brands and lot numbers should be examined to minimize this contamination.)

Extraction procedure: An extraction procedure described by Bloom (1989) was used. Depending on its concentration, weigh an approximate volume of the sample acidified to a pH of 2-5, typically 50 mL into a 125 mL Fluoropolymer bottle. If a smaller sample size is used, bring the final volume to 50 mL with DDW. Add 5 mL of 30% KCl, and swirl the bottle to mix. Add 40 mL of methylene chloride. Shake the bottle for 1-2 h with a mechanical shaker to reach a distribution equilibrium of MMHg between aqueous and solvent phases, then allow the two phases to separate. Remove the upper phase (aqueous phase) by pipetting. Add about 50 mL of DDW to the methylene chloride, and place the uncapped bottle in a hot water bath at 60° C until all of the CH_2Cl_2 has boiled away. Be aware that the methylene chloride can boil suddenly in bursts, sending water and solvent into nearby bottles. Slowly bringing the bath up to temperature can hinder this effect. Watch the bottles to see if a steady boiling arises; if not, try rearranging the bottles (heat may be unevenly distributed on the bath floor if using an electric skillet). After all visible solvent has evaporated, continue heating for ten minutes. Then purge the water for 2-3 minutes at 250 $mL \cdot min^{-1}$ with Hg free

N_2 to remove any residual solvent. The MMHg is transferred to the DDW matrix, which is ready for ethylation as described above.

7.2. Preparation of biological materials and sediments for MMHg.

7.2.1. Alkaline digestion: Weigh about 0.1 gram of biological material (wet, homogenous) into a 2.5 mL Fluoropolymer vial. Add 1.0 mL of 25% KOH methanol solution and cap the vial tightly. Digest the sample in an oven at 65° C for 3-4 hours. Avoid heating overnight, as recoveries drop sharply; recoveries may return to expected levels after sitting for several hours at room temperature. After digestion, bring the final volume to 2.5 mL with methanol prior to analysis. Analyze an appropriate aliquot, depending on the sample's concentration of MMHg and Hg(II). The day of analysis (if different from day of preparation), samples should be shaken thoroughly, heated in the oven at 65° C for 15-20 minutes and aliquots analyzed after samples have cooled and particulate settled. Alternatively, the digestion may be scaled up if larger volumes are required. One gram may be weighed into a 25.6 mL vial, and 10 mL of 25% KOH methanol solution added prior to digestion. Special care must be exhibited with biota certified reference materials as the fine particulate material can interfere with the analysis causing low recoveries. Sufficient time must be given for the fine particulate material to settle without allowing the CRM preparation to cool too much.

7.2.2. Distillation: Sediment samples should be distilled directly by weighing an appropriate amount, typically 1 gram, into a 25.6 mL Fluoropolymer vial and adding 15 mL of DDW. Distill as per the procedure mentioned above (7.1.1). If for biological samples, the MMHg concentration compared to Hg(II) is low, matrix interference on ethylation reaction caused by using large volumes of alkaline digestate will occur. This interference is avoided by distillation (Horvat, Bloom, and Liang, 1993). Distill after alkaline digestion by transferring 0.5-2.0 mL of alkaline digestate into a 25.6 mL vial, adding 15 mL DDW and following the procedure outlined in section 7.1.1.

7.3. Holding times for sample preparations.

7.3.1. Distillations: Water and sediment distillates are stable for up to 48 hours if stored at room temperature and in the dark. Distillates must not be refrigerated or frozen.

7.3.2. Digestions: Biological digestates are more stable than distillates and may be stored up to seven days prior to analysis.

8. ANALYSIS

Standards, typically 0, 10, 50, 100, 250, 1000, 2000 pg for MMHg are added into reaction vessels containing 50-75 mL of DDW and 200 µl of 2M acetate buffer. For samples, add appropriate sample volumes plus DDW as necessary for a final bubbler volume of 50 to 75 mL (for sample preparation see section 7). Some acid can be carried over during distillation: Adjust pH in the bubbler to approximately 6.2 by adding 20% KOH and/or 1:1 HOAc solutions before adding buffer, if needed. (Solution should be clear or yellow in the presence of methyl red indicator.) Subsequent addition of buffer will bring the pH to the optimum range of 3.5-5.5. An aliquot of 50 µl (75 µl for biota samples) of $NaBEt_4$ is added, the 4-way valve-cap inserted and clamped, and the vessel swirled to wash any droplets back into solution. Allow the mixture to react without purging for 15 minutes. Place a trapping column in the orientation shown in Figure 1, and then purge with N_2 at a flow rate of 250 $mL \cdot min^{-1}$ (rotometer set at 35) for 12 minutes. The organomercury compounds are swept from solution and collected onto the trapping column. Then the valve is switched to pass dry gas over the column for 5 minutes, to remove water condensation from the trap. Biota samples should be allowed to react without purging for 20 minutes, purged with N_2 for 15 minutes and allowed to dry for 5 minutes. Afterwards, connect the trapping column in-line with the GC column (Fig. 2).

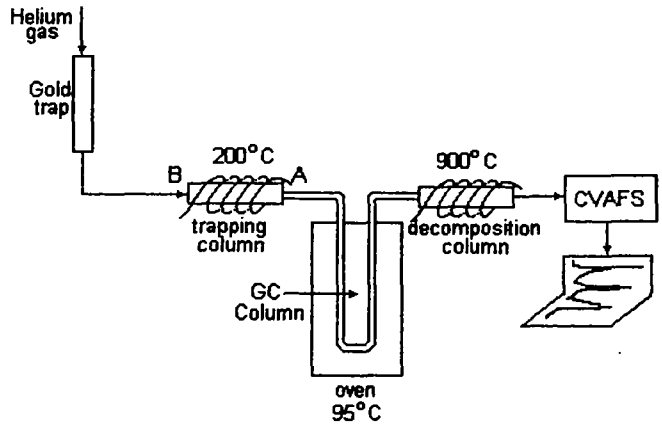

FIGURE 2: A schematic diagram of isothermal gas chromatograph system

When using a carbotrap, special attention must be paid to the orientation of the trap shown in Figure 2. The trap is placed so that the end facing the bubbler output is now facing the GC column input to avoid the organomercury species passing through the entire length of the heating trap column and decomposing to Hg(0) (Liang, Bloom, and Bloom 1994). Under a helium flow rate of 45 $mL \cdot min^{-1}$ (rotometer set at 30), apply appropriate voltage to the coil around the column so that the column reaches 200° C from room temperature within 30 seconds. The heating is controlled by switching on a timer connected in-line, while turning on the integrator or chart recorder. The organomercury species are desorbed and carried through the GC column held in an oven at 105° C. The species elute in order of increasing molecular weight, pass through the pyrolitic column,

held at approximately 900° C at which point all organomercury species are converted into Hg(0), and detected by CVAFS. The sparging/reaction vessels must be rinsed with DDW after each use, to flush out reaction by-products which can interfere with subsequent purgings.

9. CALCULATIONS

Calculate a mean (B) "peak area or peak height of the calibration (bubbler) blank".
Calculate a mean coefficient (C)

$$C = \frac{pgHg}{PA - B}$$

where PA is the peak area or peak height of the aliquot of standard.

Calculate the concentration of each species in sample by the following formula:

For aqueous samples:

$$ng\ of\ Hg/L = \{[C\cdot(S-B)\cdot V_2/V_1]-MB\}/V_3$$

where S is the peak area of the sample aliquot, V_1 is the analyzed sample aliquot size in mL, V_2 is the final dilution volume of the distillate in mL, MB is the total picograms of the method blank and V_3 is the original sample volume distilled in mL.

$$MB = C\cdot(S-B)\cdot V_2/V_1$$

where S is the peak area or peak height of method blank in mm, V_1 is the analyzed method blank aliquot size in mL, and V_2 is the final dilution volume of the method blank distillate in mL.

For solid samples:

Solid samples are calculated in the same manner as above except that V_3 is the original sample weight digested or distilled in mg, with the result being in ng/g.

10. QUALITY CONTROL

10.1. All quality control data should be maintained and available for easy reference or inspection.

10.2. Calibration data must be composed of a minimum of 2 calibration (or bubbler) blanks and a minimum of 5 standards. Such a calibration should be run when stock

standards have been remade, conditions have changed, or initial calibration checks defined in section 8.4 do not yield acceptable recoveries.

10.3. Samples containing high analyte concentrations may be run following dilution. All peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed in the calibration curve and above the adjusted PQL if possible.

10.4. Calibration checks must be analyzed after instrument calibration (or at the beginning of analysis), after every ten sample preparations and at the end of the analytical batch. Calibration checks shall consist of a mid-level standard and a bubbler (calibration check) blank. Additionally, an initial calibration check obtained from a source independent from that used to obtain the calibration standard must be analyzed after instrument calibration (or the beginning of analysis). The calibration check standard and independent calibration check standard must be within 20% of the calibration and the calibration check blank must contain no more than 2.0 pg MMHg.

10.5. Method detection limits for each preparation method and/or matrix are determined by 40 CFR 136, Appendix B using a minimum of seven replicate analyses of an appropriately prepared matrix.

10.6. A minimum of 2 method blanks per batch of 20 client samples must be run. Method blank results are entered into a quality control chart and trends are monitored. An alternative method detection limit may be obtained using the standard deviation estimated from at least 7 sets of method blanks. Method blanks should consist of all reagents used for a sample and should be carried through the entire method as a sample. To estimate the standard deviation from multiple sets of duplicate method blanks, the following formula is used:

$$\text{Estimated Standard Deviation} = \sqrt{[\sum (d \cdot d)] / 2m}$$

where d is the difference between within batch determinations of the method blanks and m is the number of duplicate blank determinations.

10.7. Method duplicate analysis should be performed for solid samples once per every 10 client samples or once per batch, whichever is greater. Duplicate samples are defined as a homogenized client sample that is split into two aliquots, and then each aliquot is carried through the entire preparation and analytical procedure. The criterion for duplicate sample precision is determined by control charts. If control charts are not available then the duplicate sample results must have a relative percent difference $\leq$ 35% or $\pm$ the PQL for water and $\leq$ 35% or $\pm$ two times the PQL for solids for the analysis to be considered valid. Precision results not meeting these criteria shall be reprepared and reanalyzed or qualified at the discretion of the lab director.

10.8. NRC or NBS certified reference materials for mercury in tissues and sediments should be analyzed at a frequency of once per every 10 client samples or once per batch, whichever is greater. Criteria for CRM recoveries are determined by control charts. If control charts are not available then CRM results should be within 35% of the certified value for the analysis to be considered valid. CRM accuracy results not meeting this criterion shall be reprepared and reanalyzed or qualified at the discretion of the lab director. Currently, there are not any water based CRMs available.

10.9. Matrix spike/matrix spike duplicate analysis should be performed once per every 10 client samples or once per batch, whichever is greater. A matrix spike sample is defined as an aliquot of homogenized sample that has a known amount of analyte added to it. The matrix spike sample is then processed through the entire preparation and analytical procedure. Bias is then determined by calculating the percent recovery of the known amount.

Percent recovery = 100 • (spiked sample result (conc.) - sample result (conc.)) / (amount spiked)

The criterion for spike recovery is determined by control charts. If control charts are not available then the spike recovery must be within the range 65-135%. Matrix spike duplicate samples may be analyzed at the request of the client. The criterion for spike duplicate sample precision is determined by control charts. If control charts are not available then the spike duplicate sample results must have a relative percent difference of 35% or less for water and 35% or less for solids for the analysis to be considered valid. Precision and accuracy results not meeting these criteria shall be reprepared and reanalyzed or qualified at the discretion of the lab director.

REFERENCES

Liang, L.; Bloom, N.S.; and Horvat, M. (1994) "Simultaneous Determination of Mercury Speciation in Biological Materials by GC/CVAFS After Ethylation and Room-Temperature Precollection." *Clin. Chem.* 40/4: 602-607.

Bloom, N.S. (1989) "Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection." *Canadian Journal of Fisheries and Aquatic Sciences.*

Long, S.J.; Scott, D.R.; and Thompson, R.J. (1973) "Atomic Absorption Determination of Elemental Mercury Collected from Ambient Air on Silver Wool." *Anal Chem.* 45: 2227-2233.

Horvat, M.; Liang, L.; and Bloom, N. (1993) "Comparison of Distillation with Other Current Isolation Methods for the Determination of Mercury Compounds in Low Level Environmental Samples., Part II: Waters." *Analytica Chimica Acta* 282:153-168.

Horvat, M.; May, K.; Stoeppler, M.; and Byrne, A.R. (1988) *Appl. Organomet. Chem.* 2: 515.

Horvat, M.; Bloom, N.; and Liang, L. (1993) "A Comparison of Distillation with Other Current Isolation Methods for the Determination of Mercury Compounds in Low Level Environmental Samples, Part I: Sediments." *Analytica Chimica Acta* 281:135-152.

EPA Draft Method 1630 (January 2001) "Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS."

EPA Method 1669 (April 1995) "Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels."

CONFIDENTIAL

MM-Hg Method BR-0011 (CVAFS)

Revision #: 007

Batch: _____ Matrix: _____

Tracking #(s): _____ Preparation Date: _____

Project #(s): _____ Prepared By: _____

QA: _____ Page _____ of _____

Sample I.D.	Aliquot (mL) / (mg)	Sample I.D.	Aliquot (mL) / (mg)

Matrix Spike/Matrix Spike Duplicate

Sample I.D.	MMHg Standard I.D.	MMHg Standard Conc. (ng/mL)	MMHg Standard Vol. used (mL)	Matrix Spike Conc. (ng/L) / (ng/g)

Quality Control Sample (QCS)

QCS I.D.	LFB/CRM I.D.	LFB/CRM Conc. (ng/L) / (ng/g)	LFB/CRM Vol./Mass (mL)/(mg)

KOH in Methanol Reagent I.D. # (Biota): _____

Final Dilution Volume: _____

Comments: _____

_____

_____

MMHg Analysis Sheet

☐MMHg ☐Other:_____ Batch:_____ Matrix:_____

Analyst:_____ Calibration Blank $\bar{X}$:_____ Blank Corr. Calib. Coef. $\bar{X}$:_____

Date:_____ Method Blank $\bar{X}$:_____ Pretrap:_____ RSD:_____

Instrument ID #_____ Standards 1 ng/mL:_____ Buffer:_____ N=:_____

QA: Full☐ Standard☐ 0.1 ng/mL:_____ $NaBEt_4$_____ r:_____

Run	Trap	Sample ID	Sample vol/wt.	Dilution Volume	Analyzed volume	Raw PA	pg	Result

Calculation Equation:_____

Comments:_____

Independent Source Std.:_____ Method SRM:_____

MMHg Analysis Sheet

Batch:_____ Analyst:_____ Date:_____

Run	Trap	Sample ID	Sample vol/wt.	Dilution Volume	Analyzed volume	Raw PA	pg	Result

Comments:_____

METHYLMERCURY EXAMPLE ANALYTICAL RUN SEQUENCE
(minimum frequency requirements)

RUN	Analyze	Description	Requirements
01	Calibration Blank (CB)		≤2.0 pg
02	Calibration Blank (CB)		≤2.0 pg
03	Calibration Blank (CB)		≤2.0 pg
04 05 06 07 08	10 pg std. 50 pg std. 100 pg std. 250 pg std. 1000 pg std.*	Calibration Curve*	Correlation Coefficient r > 0.995 RSD≤15%
09	mid-level calibration check	Independent Source	80 – 120% recovery
10	mid-level calibration verification (ICV)	Standard Source	80 – 120% recovery
11	Initial Calibration Blank Check (ICB)		≤2.0 pg
12	Method Blank 1 (MB-1)	Method Blank	Calib blank corr. conc. ≤MDL
13	Method Blank 2 (MB-2)	Method Blank	Calib blank corr. conc. ≤MDL
14 15	CRM-1 CRM-2	Reference Material	Refer to current CQAP for accuracy control limits
16	Sample 01	Native Sample	
17	Sample 01MD	Matrix Duplicate	RPD ≤ 35% for water and solid
18	Sample 02	Native Sample	
19	Sample 02MS	Matrix Spike**	Refer to current CQAP for accuracy control limits
20	Sample 03		
21	Sample 04		
22	mid-level calibration verification (CCV)	Standard Source	80 – 120% recovery
23	Blank Check (CCB)		≤2.0 pg
24	Sample 05		
25	Sample 06		
26	Sample 07		
27	Sample 08		
28	Sample 09		
29	Sample 10		
30	Sample 11	Native Sample	
31	Sample 11MD	Method Duplicate	RPD ≤ 35% for water and solid
32	Sample 12	Native Sample	
33	Sample 12MS	Matrix Spike	Refer to current CQAP for accuracy control limits
34	CCV	Standard Source	80 – 120% recovery
35	CCB		≤2.0 pg
36	Sample 13		
37	Sample 14		
38	Sample 15		
39	Sample 16		
40	Sample 17		
41	CCV	Final Calib. Check – Standard Source	80 – 120% recovery
42	CCB		≤2.0 pg

* Calibration Curve may be adjusted depending on expected range of samples (i.e. seds and biota 10pg-5000pg)

** Clients may request MS and/or MSD (Matrix Spike Duplicate), in which case lab personnel will be notified.

COPY

SOP #BR-0300

Receipt of Samples

Brooks Rand, Ltd.

Written 3/9/93
Revised 7/17/01

Revision 005

Reviewed _____

_____

_____

_____

R. Mangan	12/21/01
Operations Manager	Date
F. McFarland	12/12/01
QA Manager	Date
	12/12/01
Senior Scientist	Date
Tiffany Koo	7/17/01
Scientist (if applicable)	Date

Receipt of Samples

1. DESCRIPTION
   A. Definition: Documenting the arrival and status of samples.

   B. Scope: To ensure all samples and necessary information is present, and any discrepancies are noticed and quickly resolved.

   C. Summary: When samples arrive the samples custodian or the designated alternate checks and documents sample conditions, assigns BRL sample identification numbers, logs all sample information into the BRL "Tracking" database, preserves, and stores all samples.

2. EQUIPMENT
   A. Electronic Sample Receiving System: Consisting of PC computer with MS Access® and BRL "Tracking" Database.

   B. Sample Receiving Log Book: Three ring binder for storage of up to 100 original, computer generated sample receiving log sheets.

   C. Sample Storage Areas: Refrigerator or freezer for solid samples and refrigerator or non-metal cabinet for water samples.

   D. Preservation Reagents: HCl, BrCl, H_2SO_4, HNO_3 etc. for preserving water samples.

3. PROCEDURE
   A. Sample Analysis Request: Clients are requested to notify the Project Manager or Sample Custodian prior to sample shipment. Any time the sample custodian is not available the designated Alternate Sample Custodian must perform the work. Both the Sample Custodian and Alternate Sample Custodian are referred to as Sample Custodian for the remainder of this SOP. Clients are requested to fax the Chain of Custody (C.O.C.) or other sample identification documentation to BRL at the time they send samples. This allows the Sample Custodian to be prepared for the receipt of samples the following day. The client may send the C.O.C. form along with the sample shipment instead of faxing the form if they so choose.

   B. Sample Receiving: Samples are delivered to the sample receiving door. The Sample Custodian then documents all information on the sample receiving log form (see Exhibit A) in the BRL "Tracking" database. To obtain this information, the sample custodian checklist (see Exhibit B) should be followed and filled out during the process of receiving.

   Before the sample shipping container is opened, its condition should be documented as either being intact or any damage should be described. The custody seal (if present) information should also be recorded before opening the container. The airbill should be removed from the cooler and kept for documentation. The shipping container is then opened. All samples, regardless of whether they are known to be non-hazardous or not, are unpacked in the fume hood located in the northeast corner of the downstairs

laboratory. It is up to the Project Manager or designee to let the Sample Custodian know if hazardous samples are to arrive, and the specific hazards associated with them.

Sample bottle conditions include both temperature conditions and physical conditions (either intact or a description of the problem(s) with samples). It is very important that the Sample Custodian is aware of the preferred condition for the samples. Solid samples should be received dried, cold or frozen. Water samples should be shipped on ice and received cold. Generally, the preservation temperature of solid and water samples should be less than 4°C. The temperature of the cooler should be taken and recorded by placing a thermometer inside the cooler or in a temperature blank (provided by the client), closing the lid, and allowing the temperature to equilibrate. After this time, the cooler should be reopened and the temperature recorded.

Teflon sample bottles (for water) are engraved with a unique bottle ID number, which can be used for sample identification. When a bottle is removed, the number engraved on the bottle should be matched with the number written on the bag. All information on sample bottles (or tags) should be checked against the C.O.C. or other documentation provided by the client. If this information does not match or any other significant problems are observed (e.g. sample bottle not intact), a non-conformance form (see SOP #BR-1204) should be filled out and the Project Manager should be notified. It is then the Project Manager's duty to contact the client to resolve discrepancies. Minor discrepancies (e.g. sample received outside of preservation temperature or time) can be noted on the non-conformance form and resolved by the Project Manager at a later time.

C. EPA Sample Log-In Sheet (Exhibit C EPA form DC-1): This form must be filled out during receipt of EPA samples when required by the client. The Project Manager will notify the Sample Custodian when this form is required. Each section is completed by either filling in the appropriate information where asked, or circling the appropriate choice. If any of the items/descriptions marked with an * are circled the Sample Management Office (SMO) must be contacted and the discrepancy resolved. A record of resolution then must accompany this sample log-in sheet.

D. Preservation: If any filtration or volatile mercury analysis of water samples is required, this should be performed before preservation of samples (see SOP BR-0104 for filtration and Draft SOP BR-0005 for volatile mercury analysis). All samples should be preserved in accordance with the preservation instructions in each appropriate analytical methodology or in accordance with the client's requirements (see Exhibit D for an outline of preservation instructions). Typically, water samples that arrive for only total Hg, EPA method 1631, analysis are preserved with 0.5% BrCl. Water samples for only MMHg analysis are preserved with 0.8% HCl. Samples for Se and/or Se speciation are typically preserved with 0.8% HCl to pH < 2. Samples for As and/or As speciation are also preserved with 0.8% HCl and typically stored at 4° C. Solid samples do not need acid preservation but are preserved by being stored at <-10°C. The Project or QA Manager should be consulted if there is any question regarding sample preservation. For all water samples requiring acidification for preservation, the pH should be checked and

documented as being less than pH 2. All preservation components should be documented including the lot number of the reagent, the type of reagent, and amount used.

E. Entering the Sample into the Database: For each current project, the Project Manager maintains an active file of information specific to the project in the BRL "Tracking" MS Access database. When logging in samples, the Sample Custodian checks the contract information against the samples received to ensure that the work has been authorized and to ensure that there are no discrepancies between the work contractually approved by the client's accounting department and the work requested by the client's sampling team. If any discrepancies are found, the Project Manager should be immediately notified.

In the "Tracking" MS Access database, the samples are given a unique sample identification number as outlined by SOP #BR-0302. The sample ID number, bottle number, sample matrix, bottle size and analysis requested should be entered for each sample into the database. Once the information for the samples is completely entered in the database, the sample receiving log should be printed out along with the labels for the samples and an "Internal Custody for Original Samples" sheet. The Sample Custodian prints out a copy of the "Internal Custody for Original Samples" form found in the MS Access® Tracking database. This form is kept with the samples throughout their lifespan, from receipt to disposal. (See BR-0301, "Sample Custody and Maintenance")

F. Storage: After samples have been preserved, entered into the database, and labeled, they are stored in the appropriate sample storage locations along with the "Internal Custody for Original Samples" form. The Sample Storage Rooms (#1 and #2), the shop Freezer (#2), and the Sample Storage Cabinets (#1 through #8) each have a clear plastic folder to hold Internal Custody forms. Each time the samples are removed from their place of storage, it should be documented on the form, and the form is to remain with the samples at all times. See BR-0303, "Sample Storage and Disposal" for further information on sample storage.

Water samples requiring Hg analysis are usually stored in Storage Cabinet #1 through #7; most other analytes require refrigeration and are stored in BRL Refrigerator #2 or #3. Sediment and biota samples are generally preserved by freezing and are stored in BRL Freezer #4. All high level or hazardous samples must be clearly labeled as such and stored according to their hazard (i.e. flammable samples stored in a secured flammable storage cabinet, or high level mercury samples stored separately from low-level mercury samples--see SOP BR-0303).

G. Document Control: After samples are logged-in and stored, all sample information is place into a folder. The sample information includes the following: the C.O.C., a copy of the BRL Sample Receiving Log, the original airbill, a copy of the airbill, and the non-conformance form (if applicable). The folder should be labeled with the tracking number, the project reference number, the date received, and the due date. The folder is then given to the Project Manager for review prior to being faxed to the client and filed in the "Active Customer" file located in the Project Manager's office. Information for each current project is kept in the "Active Customer" files and is sorted alphabetically by the project reference number. Also included in the "Active Customer" file is a form to track the

number of bottles shipped to the customer and the number of bottles returned (see Exhibit E). The Sample Custodian needs to record the quantity and size of Teflon bottles sent to the client, as well as track the bottles as they are received.

The original BRL Sample Receiving Log sheets should be kept in a three ring binder at the sample receiving desk. After Sample Receiving Log sheets accumulate up to 100 tracking numbers, the Sample Custodian should bind these originals in the velo-binder and store them with the rest of the previously bound receiving sheets in the back laboratory.

Brooks Rand, LTD. Sample Receiving Log

Tracking #

Customer:
Contact:
Project Ref. #:

Collection Date
QA Level

Sample Condition
Shipping container intact?

Shipping container type:
Shipping container temp:
Shipping container coolant:

Sample preservation:
Acid lab #
Hg Concentration:
Sample storage area:

Sample Turnaround Time:
Contract Turnaround Time: days

Comments:

Due Date:
Receiving Date:
Receiving Time:

Logged-in by:
Log-in Date:
Log-in Time:

Airbill present?
Airbill #
Carrier:

Custody seal present?
Custody seal intact?
COC Present?
COC Number:

Case #:
SDG #:

Analysis request form?

COC/Sample log agree?

Lab ID:	Sample Tag #	Container #	Size:	pH	Matrix/Sub-Matrix	Comments:
					#Error	

Analysis / Method:

Sample Custodian signature Date

Sample Custodian Checklist

Type of Shipping Container:	Cooler	Cardboard Box			Other_____
Condition of Shipping Container:	Intact	Damaged*			
Custody Seal Present:	Yes	No			
Custody Seal Intact:	Yes	No*			
Type of Coolant:	Blue Ice	Ice	Dry Ice	None	
Temperature:	_____°C**				
C.O.C. Present:	Yes	No			
C.O.C. Signed:	Yes	No	N/A		
ARF Present:	Yes	No			
Condition of Sample:	Intact	Damaged*			
Sample Tags Agree w/ COC/ARF:	Yes	No*			
Bottle/Container:					
Type:	Teflon	Poly	Glass	Other_____	
Size:	_____mL				
Teflon Bottle #s:	_____				
Bottle Custody Seals Present:	Yes	No			
Airbill Present:	Yes	No	N/A		
Carrier:	UPS	FedEX	Airborne	Hand-delivery	Other_____
Preservation:					
Chemical:	_____				
Concentration/Percentage:	_____				
ID #:	_____				
Final pH of Samples:	<2	Other_____			
Storage Location:	Cab #1	Cab#2	Cab#3	Fridge#2	Freezer#4 Other_____
BRL Labels:	Completed				
Internal Custody for Original Samples:	Completed				
Bottle Accounting:	Recorded				
Faxing:	Completed				
Filing:	Completed				

* fill out non-conformance form
** if temperature >4°C for sediment/biota/water samples, fill out non-conformance form

Brooks Rand Log-in Sheet
for EPA samples

BR-0300 -8
Revision 005
Exhibit C

Received By (Print Name): ______________________ Log-in Date: __________ __________

Recieved By (Signature): ______________________________________ ______________________________

	EPA SAMPLE #	CORRESPONDING SAMPLE TAG #	ASSIGNED LAB #	REMARKS CONDITION OF SAMPLE SHIPMENT, ETC.
Case Number: ______________				
Sample Delivery Group No.: ______________ ______________				
SAS Number: ______________				
REMARKS:				
1. Custody Seal(s) — Present/Absent* Intact/Broken				
2. Custody Seal Nos.: ______________ ______________				
3. Chain-of-Custody Records — Present/Absent*				
4. Traffic Reports or Packing List — Present/Absent*				
5. Airbill — Airbill/Sticker Present/Absent*				
6. Airbill No.: ______________ ______________				
7. Sample Tags — Present/Absent*				
Sample Tag Numbers — Listed/Not listed on Chain-of-Custody				
8. Sample Condition: — Intact/Broken*/ Leaking				
9. Does information on custody records, traffic reports, and sample tags agree? — Yes/No*				
10. Date Received at Lab: ______________				
11. Time Received ______________				
Sample Transfer				
Fraction: ______________ ______________				
Area #: ______________ ______________				
By: ______________ ______________				
On: ______________ ______________				

*Contact SMO and attatch record of resolution
Reviewed By: ______________________
Date: ______________________

FORM DC-1

Logbook No.: ______________________
Logbook Page No.: ______________________

Analysis to be Performed	Preservative*	Holding Period (after preservation)	Container
□ H_2O			
Hg-Total, EPA 1631	0.5% BrCl	28 days	Teflon, Glass
Hg-Total, EPA 245.1	0.2% HNO_3	28 days	Teflon, Glass
MMHg-& Hg-Tg	0.8% HCl	28 days	Teflon, Glass
Se-Total, BR-0020 As-Total, BR-0020	0.8% HCl	28 days	Poly Bottle, Teflon, Glass
As(III), As(V), MMAs, DMAs BR-0021	0.8% HCl & 4°C	28 days	Poly Bottle, Teflon, Glass
Se(IV), Se(VI), BR-0023	0.8% HCl & 4°C	28 days	Poly Bottle, Teflon, Glass
All Metals, EPA 200.9	0.4% HNO_3	6 months	Poly Bottle, Teflon, Glass
*** ALL WATER SAMPLES CHECK pH < 2**			
□ Sediment			
As(III), As(V), MMAs, DMAs BR-0021	4°C	5days	Teflon, Glass
Hg-T, MMHg, As-T, As(inorg) Se-T	< -10°C	1 yr	Teflon, Glass
□ Biological			
Tissues	< -10°C	1 yr	Teflon, Glass

BR-0300 -10
Revision 005
Exhibit E

Brooks Rand, Ltd.

Teflon Bottle Accounting Form
Revision 002
3/29/01

Project #_____

Teflon	Shipping		Receiving		Receiving		Receiving		Difference
Size (mL)	Date	Quantity	Date	Quantity	Date	Quantity	Date	Quantity	Quantity

COPY

SOP #BR-0301

Sample Custody Maintenance and Tracking

Brooks Rand, LLC

Written 3/15/93
Revised 6/10/02

Revision 004

Reviewed _____

_____

_____

_____

_____	11/14/02
President	Date
_____	10/18/02
QA Manager	Date
_____	10/18/02
Senior Scientist	Date
_____	_____
Scientist (if applicable)	Date

Sample Custody Maintenance and Tracking

1. DESCRIPTION
   A. Definition: Maintaining and documenting possession and integrity of samples from receipt through disposal.

   B. Scope: Maintaining sample custody ensures sample integrity, data defensibility and documents tracking of samples through their entire life cycle.

   C. Summary: Sample custody is ensured by means of proper identification, tracking and security of samples, and all changes in custody are documented.

2. SAMPLE SECURITY
   A. Samples are identified as described in SOP BR-0302, *Sample Identification*. All samples are stored in accordance with the specific preservation and storage requirements outlined in the pertinent analytical SOPs (SOP #s BR-0001 through BR-0099) and in SOP BR-0303, *Sample Storage and Disposal*.

   B. All samples are labeled when received with the client project number, the date of receipt, the preservation, and the BRL sample identification number. Sample identification labels are kept on the sample containers at all times.

   C. Samples are kept in the custody of the responsible employee or in the custody of a secured sample storage area.

      Sample custody is defined as:
      the sample is in your possession, or
      the sample is in your view after it has been in your possession, or
      the sample was in your possession and you locked the sample in a secure area.

   D. The secure areas of Brooks Rand, LLC (defined as areas accessible to authorized personnel only) are as follows:
      Sample Storage Cabinets: located in the downstairs lab on the South facing wall. Cabinets are non-metallic (wood). Samples to be stored in this location include all original samples suitable for storage at room temperature.

      Sample Storage Room #1: located off of the hallway leading to the downstairs bathroom (Southmost corner of the building). This sample storage room contains BRL Refrigerator #2 and Freezer #4, and will be used for all samples (original and preparations) requiring cold storage of either 4°C or <-10°C.

      Sample Storage Room #2: located adjacent to Sample Storage Room #1. This sample storage room will be used to store all sample preparations and performance evaluation (PE) samples suitable for storage at room temperature.

Freezers #2: These freezers are located in the NW corner of the downstairs and will be used for long term storage (archival) of original solid samples after analysis is complete. BRL policy is to archive client solid samples for a minimum of one year prior to disposal.

All visitors are required to sign-in at the front door and must be accompanied by a laboratory employee while in the laboratory. A copy of the visitor sign-in log sheet is included as exhibit A. The laboratory is kept locked outside of normal business hours.

In addition to the above mentioned sample custody maintenance steps, each stage of the process for a batch of samples is documented on the Sample Processing Form (see SOP # BR-0304) and is logged in on computer by the responsible employee. This serves as a further tracking device to monitor sample status.

3. PROCEDURE FOR TRACKING CUSTODY OF ORIGINAL SAMPLES

When samples are received, a "Internal Sample Custody for Original Samples" form shall be filled out (see Exhibit B). Original samples shall be tracked by the tracking number assigned to them upon receipt. This tracking number and the client project # is documented on the custody form. In addition, all activity (receipt), location (sample receiving), initials, date, and time shall be recorded in respects to the sample IDs. Once samples have been logged in, the samples are transferred to the appropriate storage location. The custody form is then used to document Activity (storage), location (i.e. sample storage cabinet), initials, and date and time of custody transfer. The custody form is then placed in the holder located on the outside of the sample storage location.

Whenever samples are removed from the storage location for sample processing (i.e. sample preparation), the custody form is then used to document this custody transfer. Similarly, when this activity is completed and samples are transferred back to storage, this is also documented. When samples are disposed of this information is documented on the custody form as the last entry.

In summary, every transfer of custody should be documented. Custody forms must always accompany the set of samples either physically with the samples when they are in the possession of an analyst or in the holder when they are in storage.

4. PROCEDURE FOR TRACKING CUSTODY OF SAMPLE PREPARATIONS

When samples are being prepared, a "Internal Sample Custody for Sample Preparations" form (See exhibit C) must be generated. Documentation on this form shall include the Batch number, analyte and analytical method number, sample ID numbers, activity, location, initials, date and time. Each time custody is transferred (either to another employee or to storage), the activity, location, initials, date and time are documented.

5. QUALITY ASSURANCE

Each person is responsible for filling out the appropriate information for the activity that they performed. Upon disposal of a set of samples, the custody forms of the original samples and

the sample preparations are then considered complete and filed away for document archival in the Document Storeroom.

Exhibit A

Brooks Rand, LLC
Visitor Sign-in Sheet

Date	Visitor Name	Company	Employee Contact	Time In	Time Out

INTERNAL CUSTODY FOR ORIGINAL SAMPLES

Tracking #: Project Reference #:

Activity								
Location								
Initials								
Date								
Time								
Sample ID								

INTERNAL CUSTODY FOR SAMPLE PREPARATIONS

Batch #: Analysis: Method #:

Activity									
Location									
Initials									
Date									
Time									
Sample ID									

COPY

SOP #BR-0303

Sample Storage and Disposal

Brooks Rand, LLC

Written 3/15/93
Revised 10/10/02

Revision 004

Reviewed _____

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_____

_____

_____	11/11/02
President	Date
_____	10/21/02
QA Manager	Date
_____	10/24/02
Senior Scientist	Date
_____	_____
Scientist (if applicable)	Date

Sample Storage and Disposal

1. DESCRIPTION
   A. Definition: The location and duration of storing samples, documentation and disposal.

   B. Scope: To ensure the integrity of the samples, and to ensure proper disposal of samples and sample waste.

   C. Summary: Water samples are stored in the designated non-metal cabinet or refrigerator. Solid samples are stored in a calibrated freezer for at least one-year unless otherwise specified by the client. Samples are disposed, once approval is obtained, and disposal is documented.

2. EQUIPMENT
   A. Storage facilities and Equipment: Calibrated freezers, calibrated refrigerator, non-metal storage cabinet

   B. Disposal Facilities and Equipment: Disposal containers (30 gallon drums and 5 gallon buckets) and spill containment equipment

3. STORAGE
   A. Receipt: Samples are received in the downstairs laboratory (see SOP BR-0300, Receipt of Samples). Prior to storage, an "Internal Custody for Original Samples" form is created for each shipment, which will document each step of a sample's life cycle--from receipt to disposal. Similarly, an "Internal Custody for Sample Preparations" will be created for each group of samples as they are batched for analysis preparation, documenting the life cycle for each batch of preparations. (See BR-0301, "Sample Custody Maintenance.")

   B. Water samples: Water samples are preserved when received (see SOP BR-0300). After receipt, samples are stored in the designated storage cabinets or refrigerator (unless otherwise requested by the client or lab manager) until they are transferred to other personnel for preparation or analysis. On occasion, it may be necessary to store samples in Sample Storage Room #2 due to the limited storage capacity of the sample storage cabinets. The designated storage cabinets at Brooks Rand are located in the downstairs front laboratory in the southeast corner above the counter, and are marked and identified as "Sample Storage Cabinet #1" and "Sample Storage Cabinet #2". These cabinets should only be opened when necessary to minimize UV exposure and to restrict airflow and particulates. All water samples are stored for a minimum of one month from the time of receipt at Brooks Rand, unless requested otherwise.

   C. Solid samples: After receipt, solid samples are stored in the freezer located in Sample Storage Room #1 (BRL Freezer #4). After samples have been analyzed

and the data is reviewed and deemed acceptable, the remaining portions are stored in one of the freezers located in the downstairs northwest corner of the building for long term storage (Freezer #2). Solid samples are stored for a minimum of one year from the time of receipt unless requested otherwise.

D. Air samples: Air samples collected on traps should be stored in a ziplock bag with the Teflon caps on the ends. The bagged traps can be stored at room temperature in Sample Storage Room #2 until analysis. Organic mercury samples on carbon traps should be analyzed within three days from collection. Total and elemental mercury samples collected on gold-coated silica traps can be stored for up to three months before analysis. For air samples collected on either carbon or gold coated silica traps, once the trap has been analyzed there is no sample remaining and therefore there is no storage for samples after analysis.

E. Volatile analysis: Samples for analysis of volatile mercury species are kept at 4°C in BRL Refrigerator #2 until analyzed. These analyses should be performed within 48 hours of sample collection. Once the analyses are complete, these samples should be treated appropriately depending on remaining analyses. If any further analyses are to be performed, the samples should then be preserved and stored appropriately.

F. Sample preparations: After preparation, each sample batch will be stored in Sample Storage Room #2 until analysis. After the batch has been analyzed, the sample batch will be returned to Sample Storage Room #2 until the lab manager releases them for disposal.

G. High level and hazardous samples: Brooks Rand must be notified if samples are suspected to be high in mercury or other analytes. All samples determined (or suspected) to be extremely high level, must be stored separately in a secure storage area outside of the analytical laboratory to ensure cross-contamination of the clean lab or other samples does not occur. Sample Storage Room #2 may be used for high level samples provided that there are no low-level water samples or preparations being stored in this storage room at the same time. BRL Freezers #2 or BRL Refrigerator #2 may also be utilized for high-level sample storage (depending on the sample matrix). If a client notifies BRL that samples may be hazardous in properties that would not contribute to clean lab contamination, but could possibly compromise worker safety, those samples must be handled as hazardous. All high level or hazardous samples must be clearly labeled as such and stored according to their hazard (i.e. flammable samples stored in a secured flammable storage cabinet, or high level mercury samples stored separately from low-level mercury samples). All laboratory workers receive yearly Right-To-Know training; in addition, at least one laboratory worker should be trained in the handling of hazardous waste, and will provide yearly training to other workers in the proper safe handling procedures for hazardous substances (see the BRL Chemical Hygiene Plan for further details).

4. SECURITY

The secure areas of Brooks Rand, LLC (defined as areas accessible to authorized personnel only) are the analytical laboratories, the designated sample storage cabinets, the sample storage freezers, and the sample storage rooms. All visitors are required to sign-in and must be accompanied by a laboratory employee while in the laboratory. The laboratories and office spaces are kept locked outside of normal business hours. The sample storage rooms and cabinets are unlocked only to retrive samples or sample preparations, but are otherwise kept locked at all hours.

5. HANDLING OF SAMPLE PREPARATIONS

A. After a batch is analyzed, the preparations for a batch shall be stored in Sample Storage Room #2, clearly labeled with the batch number, and stored in such a way that the batch is kept intact and separate from samples in other batches. This will enable the Sample Custodian to easily locate the specific batches that have been designated for disposal.

B. Occasionally, Brooks Rand LLC will receive samples that are known to contain dangerous properties other than the metals listed above. One example is a sample known to contain background levels of radioactivity (See SOP #'s BR-1600 and BR-1601 for Low Level Radioactive Waste storage and packaging for disposal). The sample preparations for hazardous samples should be clearly marked at the time of preparation for the safety of lab employees and so that the sample custodian may dispose of the preparations in a manner consistent with the disposal of the original samples.

6. DISPOSAL (or TRANSFER)

A. Sample Preparations: Once samples have been analyzed, reported, and either the data has been reviewed to be acceptable or has been determined that there is no value in reanalyzing the sample preparations, the sample preparations may be disposed. Sample preps may also be transferred for long time storage, upon client's request. The Lab Manager (or designee) will notify the Sample Custodian of any batches ready for disposal or transfer. The Sample Custodian shall retrieve the appropriate batch(es) and dispose or transfer the sample preparations accordingly (see Section 6C). The disposal of each batch shall be documented on the "Internal Custody for Sample Preparations" form (see section 7).

B. Original Samples: After completion of a report for a particular set of samples (one or more tracking numbers), the original samples may be either transferred to long-term storage or disposed of, if approved by the Lab Manager or the client. The Lab Manager will notify the Sample Custodian which original samples to dispose of or transfer. The Sample Custodian shall dispose (or transfer) the samples accordingly (see Section 6C). When samples are disposed, the "Internal Custody for Original Samples" log sheet should be signed off appropriately (see section 7).

C. Disposal Guidelines: Current limits for the analytes most frequently tested at BRL are as follows:

Table 1. - Disposal Limits

Analyte	Matrix	Limit (grab)	Source of Information*
As	Water	4.0 mg/L or ppm	King Co. Water Pollution Control Div.
As	Solids	5 µg/g or ppm	King Co. Solid Waste Div.
Hg	Water	0.2 mg/L or ppm	King Co. Water Pollution Control Div.
Hg	Solids	0.2 µg/g or ppm	King Co. Solid Waste Div.
Se	Water	1 mg/L or ppm	King Co. Water Pollution Control Div.
Se	Solids	1 µg/g or ppm	King Co. Solid Waste Div.

*Information updated 5/97. King County Water Pollution Control Division was formerly part of Metro.

1. Routine Disposal – Samples below the disposal limits.
   a) Water Samples and Acid Digestion - Water samples (including preparations) and acid digested solid samples that are not hazardous may be disposed of down the drain. All acidic samples must be neutralized with Soda-Ash prior to disposal. Original sample and sample preps that contained BrCl must be further neutralized with 30% hydroxalmine hydrochloric (NH_2OH-HCl). All labels identifying the client must be removed from the bottles. All neutralized samples and sample preparations that are disposed of to the sewer must be documented on the "Drain Disposal Log" sheets (Exhibit A).
   b) Native Solid Samples and Dry Weights - All native solid samples (not sample preparations) may be discarded directly into the garbage. As with the water samples, all labels with the client name must be removed from the containers.

2. High Level Disposal – Samples that are hazardous waste and must be recorded on the "Waste Disposal Log" sheets (Exhibit B). An employee certified to handle the hazardous waste containers must accompany the Sample Custodian during disposal.
   a) Water Samples and Acid Digestions - the sample material is placed directly into the high-level metals waste storage container.
   b) Native Solid Samples and Dry Weights - All native solid samples (not sample preparations) may be disposed of directly into the hazardous waste container.
   c) Solvent Extracts - All solvent extracts must be treated as hazardous waste. Solvent extracts may be consolidated in clearly marked containers near the hazardous waste fume hood, and disposed of as hazardous waste.

3. Non-Routine Disposal - Samples that are designated by the client to be high level in an analyte not performed by BRL shall be considered hazardous and treated as hazardous waste upon authorization for disposal. In certain cases,

BRL may contract with a client to analyze samples that are known to be hazardous beyond the scope of our analysis (such as samples containing a high level of organic contaminants or dioxins), these samples will be flagged as requiring special disposal - by lab manager's instruction - and disposed of through a licensed hazardous waste acceptance facility. BRL may also arrange with the client to return the leftover samples to the client after analysis.

4. High Level Metals Waste Transport and Ultimate Disposal - Once a sufficient volume of waste is generated, warranting proper disposal, a waste disposal company should be contacted, and the waste scheduled for pick-up. While it is the responsibility of the waste handling company to transport and dispose of the high metal level waste in a manner consistent with local and federal environmental laws and regulations, BRL recognizes that as the generator ultimate liability can fall on BRL, and therefore every attempt is made to ensure that our contracted TSD company properly handles, transports, and disposes of all waste generated by BRL. The hazardous waste facility currently utilized by Brooks Rand is Philip Services Corp. in Renton, WA.

5. Low-level Radioactive Waste - All samples that are required to be disposed of as low-level radioactive waste need to be disposed of as detailed in SOPs BR-1600 and BR-1601 regardless of the concentrations of metals.

6. *Special Note about Biota samples and preparations:* High-level original biota samples (such as fish) must be consolidated for hazardous disposal separately from other hazardous waste. Original biota samples (such as fish, bivalves, mammal tissue, etc.) that are below disposal limits may be discarded directly into the garbage. Hazardous biota digestates (either acidic or alkaline) do not need to be composited separately, as the tissue has been degraded enough to be treated the same as other solid digestates. However, high-level biota dry weights do need to be treated as original biota samples, as the process for dry weight preparation does not sufficiently alter the tissue composition.

E. Transferring Guidelines:

1. Sample Preps – Sample preps in Teflon vials or bottles can be transferred into ultraclean 40mL glass vials or an equivalent. Transferred samples and samples in non-Teflon containers can be put in Cab #8 for long-term storage. Cab #8 should be cleared of the sample preps once a year.

2. Original Samples - Upon a client's request, solid samples may be transferred to BRL Freezers #2 for long term storage. If solid samples are in Teflon containers, and are to be transferred, the samples should first be removed from the Teflon containers and placed in acid cleaned sample jars or other appropriate non-Teflon containers. Before moving samples to Freezer #2, all of the samples for a particular project or tracking number should be placed in a bag, and the bag should be **marked clearly with the tracking number,**

name of client and the sample receiving date. At least once a year, Freezers #2 should be cleared of any samples that are more than one year old.

7. DOCUMENTATION

Samples and preparations that are considered hazardous waste will be recorded upon disposal in the Waste Disposal Log, which is kept in a bound notebook at the sample disposal fume hood located in the shop. The "Internal Custody" sheets (SOP #BR-0301, Exhibits B and C) are used to document the disposal of samples and sample preparations as well as the transfer of samples or preparations from one location of the laboratory to another. Forms for disposed samples are filed in the back lab. Forms for transferred samples shall be kept with the samples or preparations until disposal. Special customer requirements may necessitate additional documentation, which shall be implemented as the need arises.

Drain Disposal Log for Neutralized Waters within the Acceptable Sewer Limits

Date	Initials	Volume	Notes

Brooks Rand, LLC
Waste Disposal Log

Date	Initials	Supervisor Initials	Volume Disposed	Disposal Location

COPY

SOP #BR-0304

Sample Processing

Brooks Rand, Ltd.

Written 3/16/93
Revised 6/10/02

Revision 003

Reviewed _____

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_____

_____

_____	11/11/02
President	Date
_____	10/22/02
QA Manager	Date
_____	10/22/02
Senior Scientist	Date
_____	_____
Scientist (if applicable)	Date

Sample Processing

1. DESCRIPTION
   A. Definition: Documentation of the flow of sample processing from batching of samples to final review of data.
   B. Scope: To ensure all sample requirements are completed and documented.
   C. Summary: Comments for each step of sample processing will be written on a Sample Processing Form (SPF) and initialed and dated.

2. PROCEDURE
   Note: Tracking of original samples and sample aliquots is achieved by SOP # BR-0306, *Sample Tracking*, # BR-0303, *Sample Storage and Disposal* and # BR-0300 *Receipt of Samples*. Together, these SOPs cover the documentation of the custody of samples from receipt to disposal including all processing for the actual analytical work. This SOP primarily covers the tracking and documentation of analytical sample processing and the stages of data review.

   A. Sample Batching - After samples are received and logged in (see SOP BR-0300), the samples are then batched by the Laboratory Manager. Batches are sequentially numbered starting with the last two digits of the year followed by a three digit sequential number. For example the first batch in 2001 is numbered 01-001. Batch numbers are assigned to each sample on the BRL "Tracking" database. The Sample Processing Form (SPF) is then generated for each batch of samples (see Exhibit A).

   B. Sample Preparation - The SPF is given to the scientist responsible for sample preparation. From the time the scientist removes samples from the storage area the SPF must remain with the sample batch. All sample preparation must be documented on a form or in a logbook. Copies of all preparation documentation, once complete, must accompany the SPF. The SPF must be signed and dated by the scientist performing the sample preparation, and any comments on unusual observances or deviations from the analytical SOP must be documented. The person performing the sample preparations should also update the batch status in the BRL "Tracking" database to indicate that this phase of the process is complete. After sample preparation is complete, the prepared samples, along with the SPF and preparation documentation, should be stored in the appropriate sample storage area (see SOP #BR-0303, *Sample Storage and Disposal.*

   C. Sample Analysis - When a batch of samples is analyzed, the analyst must sign and date the SPF. Any comments on unusual observances or deviations from the analytical SOP must be documented and must be referenced on the SPF. After analysis is complete, all data including the raw instrument printouts, the analytical bench sheets, and the preparation notes must be attached to the SPF. The analyst should also update the batch status in the BRL "Tracking" database to indicate that this phase of the process is complete.

   D. Raw Data Review - The scientist who analyzed the batch is also responsible for performing the raw data review. When the data is reviewed, the reviewer must sign and date the SPF and comment on any unusual observances or deviations from SOP # BR-1300. The data reviewer should also update the batch status in the BRL "Tracking" database to indicate that this phase of the process is complete.

E. Data Entry - Again, the scientist who analyzed the batch is also responsible for entering all raw data into the computer spreadsheets. After data entry is complete (see SOP # BR-1301), the SPF is signed and dated. Comments on any unusual observances or deviations from SOP # BR-1301 should be documented on the SPF. The computer result pages are not printed out at this time, but instead are reviewed in electronic format during the final review. The data package is then submitted to the QA Manager for final review. The person performing the data entry should also update the batch status in the BRL "Tracking" database to indicate that this phase of the process is complete.

F Final Review - The QA Manager reviews the final data (see SOP # BR-1303) and prints out the computer result pages which are then included in the data package. After final review, the QA Manager must sign and date the SPF and include comments on any unusual observations and/or deviations from SOP # BR-1303. The QA Manager should also update the batch status in the BRL "Tracking" database to indicate that this phase of the process is complete. The data packages are then stored in the "Active Client" file (located in the Project Manager's office) until all data is complete for a particular set of samples (as defined by the client) at which time the case narrative is prepared.

3. ADDITIONAL MEASURES

A. Incomplete analysis of a batch - If all samples included on one SPF are prepared together but not analyzed on the same day or under the same calibration curve, then this should clearly be noted on the SPF. In such an instance, all batch specific QA samples should be analyzed during each analysis to ensure that no degradation in the sample preparations has taken place. If the method specific preparation holding time is surpassed for the samples not analyzed, then each of the samples not analyzed is crossed out from the original SPF with a single line that is initialed and dated. The samples not analyzed are then rebatched using an identification number other than that used for the batch of which they were originally a part.

B. Deviation Traceability - The SPF and the *Analytical Non-conformance and Resolution* Form (see SOP #BR1204) are the primary documents used to record analytical deviation and/or problems. The SPF should contain any mention of unusual events or occurrences or deviations from SOPs and should list where this information can be found if relevant. Examples include, but are not limited to the following:

- Bad calibration curve-see lab data sheet.
- Samples not cold when removed from refrigerator-see instrument logbook.
- Samples over distilled-see distillation log sheet.
- Samples prepared different from SOP-see prep. notes.

In this way all necessary information concerning samples and all sample-handling steps can be traced and noted in the report to the customer.

4. QUALITY ASSURANCE

Each person is responsible for filling out the appropriate information for the task that they performed. The next responsible person will not accept the data and SPF unless the previous section is complete.

SAMPLE PROCESSING FORM

Batch #: Analysis: Method:

Tracking #	Lab ID	Project Ref #	Data Due Date	Matrix	Comments

QA:

Tracking # See SOW See Memo See Proj Mgr Consult MSDS See Contract Info See Lab Mgr

QA Comments

Batched By _____ Date: _____

Prepared By: _____ Date: _____
Comments: _____

Analyzed By: _____ Date: _____
Comments: _____

Data Entry By _____ Date: _____
Comments: _____

Primary Data Review B _____ Date: _____
Comments: _____

Final Review By: _____ Date: _____
Comments: _____

COPY

SOP #BR-1205

Preventative Maintenance

Brooks Rand, LLC

Written 2/25/02
Revison 000

Reviewed _____

_____

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_____

_____	02/28/02
President	Date
_____	02/26/02
QA Manager	Date
_____	2/25/02
Senior Scientist	Date
_____	_____
Lead Scientist (if applicable)	Date

Preventative Maintenance

1. DESCRIPTION
   A. Definition: All laboratory equipment undergoes routine maintenance that follows a clearly defined schedule. Routine maintenance is performed in a proactive manner in order to prevent problems from arising in the first place.

   B. Scope: BR-1205 describes the type of maintenance to be carried out, as well as the schedule of routine maintenance for each major piece of laboratory equipment and laboratory space used at BRL.

   C. Summary: Each piece of laboratory equipment undergoes routine maintenance on a daily, weekly, monthly, quarterly, semi-annual, and/or annual basis. All maintenance is documented in each equipment's instrument log and the instrument is tested prior to being used for any sample analysis.

2. EQUIPMENT
   A. Equipment List:
      - BRL Model III CVAFS Hg Detector
      - Perkin Elmer Model 703 Flame AAS Detector
      - Perkin Elmer Model 5000 GF and Flame AAS Detector
      - Perkin Elmer Model 4100ZL GF ZAAS Detector
      - Sequoia-Turner Model 690 Colorimetric Spectrophotometer
      - Perkin Elmer Model 1420 IR Spectrophotometer
      - Orion Research Model 301 pH Meter
      - VWR Pure H_2O Tester Conductivity Meter
      - Mettler Model H10 Analytical Balance (to 0.1 mg)
      - Sartorius Model E1200 Top Loading Balance (to 1 mg)
      - ACCULAB Model VI-350 Top Loading Balance (to 10 mg)
      - Mettler Model BB2400 Top Loading Balance (to 10 mg)
      - Various pipettes
      - Oven and Freezer Thermometers
      - Omega Model CN76000 Thermocoupler
      - Fisher Scientific Model 630F Scientific Oven
      - Labline Instruments Isotemp Scientific Oven
      - Forma Scientific Model 3927 Incubator/Refrigerator
      - Sears Coldspot Refrigerator/Freezer
      - Kenmore Model 20 Refrigerator/Freezer
      - General Electric Model CB22D Chest Freezer
      - Sears Coldspot Chest Feezer
      - Montgomery Ward Model FFT-4945 00L Upright Freezer

B. Various instrument logbooks

3. PROCEDURE

All laboratory equipment undergoes scheduled routine maintenance to ensure that it is functioning properly prior to being used for sample preparation or analysis. Each instrument has its own "instrument log" where all routine checks and maintenance are documented (refer to SOP #BR-1200). A copy of the overall lab maintenance schedule is presented as Exhibit A. The following sections break the schedule down into the various instrument groups utilized at Brook Rand LLC.

All listed maintenance is the minimum required. Other non-routine maintenance may be required as dictated by system performance.

A. Trace Level Mercury System (CVAFS): The trace level mercury system is located in the Clean Room Lab and it includes both instruments setup to analyze for total mercury (BRL Model III Hg Detectors #s BR-06 and BR-08) and the instrument setup to analyze for methyl mercury (BRL Model III Hg Detector #BR-05. The frequency of maintenance can be broken down into daily, weekly, monthly, quarterly, semi-annual, and annual schedules.

1. Daily: Prior to each analytical run.
   a. Check all fittings to ensure that they are secure and not leaking.
   b. Rinse and refill the DDIW bottle.
   c. Prepare new pretraps for total mercury analyses.
   d. Blank each analytical trap prior to analysis.
   e. Blank each analytical trap after each non-zero run for the methyl mercury system.

2. Weekly: Friday of each week.
   Soak bubblers over the weekend in 1% KOH solution.

3. Monthly: The last Friday of each month.
   a. Inspect all tubing for signs of wear.
   b. Replace any loose fittings.
   c. Prepare new stock standards.

4. Quarterly: The last Thursday/Friday of January, April, July, and October.
   a. Make, test, and change out traps on the total mercury system.
   b. Condition the GC column on the methyl mercury system. The column should be heated at 180° C overnight (Thursday afternoon to Friday morning). Heating the column over the weekend could significantly reduce the column's efficiency.

5. Semi-Annual: The last Friday of January and July.
   a. Replace lamps.
   b. Make, test, and change out traps on the methyl mercury system.
   c. Blank traps on the incoming gas lines (replace as needed).

6. Annual: The last Friday of January
   a. Clean/change the quartz cell.
   b. Replace GC column on the methyl mercury system.
   c. Ensure that there are backup analytical traps, mercury lamps, and Teflon tubing.

B. Hydride System (HGAAS) – Perkin Elmer Model 703: The hydride system is located in the AA Lab. The maintenance schedule is as follows.

1. Daily: Prior to each analytical run.
   a. Rinse and refill the DIW bottle.
   b. Check all fittings to ensure that they are secure and not leaking.
   c. Rinse water removal trap with DIW at the end of the analytical day.

2. Weekly: Friday of each week.
   a. Soak bubblers over the weekend in 1% KOH solution.
   b. Clean the spectrophotometer windows.

3. Monthly: The last Friday of each month.
   a. Inspect all tubing for signs of wear.
   b. Replace any loose fittings.
   c. Prepare new stock standards.

4. Quarterly: The last Friday of January, April, July, and October.
   a. Ensure that there are working traps for both arsenic and selenium.
   b. Ensure that there are backup traps for both arsenic and selenium.

5. Semi-Annual: The last Friday of January and July.
   a. Verify that there are working backup lamps for both arsenic and selenium.
   b. Clean nebulizer.

6. Annual: The last Friday of January
   a. Fine tune the instrument wavelength.
   b. Check instrument optics.
   c. Test backup lamps.

C. Graphite Furnace System (GFAAS) – Perkin Elmer Model 4100ZL: The graphite furnace system is located in the AA Lab. The maintenance schedule is as follows.

1. Daily: Prior to each analytical run.
   a. Check graphite tube.
   b. Clean furnace housing.

2. Semi-Annual: The last Friday of January and July.
   a. Change graphite contact cylinders.
   b. Document availability of lamps for each analyte.

3. Annual: The last Friday of January
   a. Test lamps (over several days) for all analytes.
   b. Ensure that all lamps are identifiable by a unique serial number so that test results can be traced back to each lamp.

D. Mercury System (CVAAS) – Perkin Elmer Model 5000: The mercury system for the analysis of samples by EPA Method 245.1 is located in the AA Lab. The maintenance schedule is as follows.

Daily: Prior to each analytical run.
1. Clean instrument.
2. Verify that instrument in working order.
3. Check supply of chart recorder paper.

E. Deionized Water System:

1. Daily: Prior to use.
   a. Test conductivity of DIW/DDIW at source in each lab.
   b. Check system pressure differential and change filters as needed. Always change filters on a Friday to allow the system to stabilize over the weekend.

2. Weekly: Friday of each week.
   Check probe cables on conductivity meter.

3. Monthly: The last Friday of each month.
   Check calibration of conductivity meter.

4. Semi-Annual: The last Friday of January and July.
   Change 0.2 µm DDIW final filter.

5. Annual: January
   a. Schedule US Filter to change out the carbon filter.
   b. Schedule US Filter to recharge the mix bed tanks.

F. Balances:

1. Daily: Prior to use.
   Check calibration over range of weights being used.

2. Monthly: The last Friday of each month.
   Conduct a four-point calibration check for each balance.

3. Annual: February
   Schedule certified calibrations for each scale.

G. Thermometers:

1. Monthly: The last Friday of each month.
   a. Check thermometers for wear.
   b. Check thermal couplers on sand baths for wear.
2. Annual: October
   a. Schedule certified calibrations for NIST certified thermometers:
      i. VWR 61054-546 refrigerator/freezer thermometer
      ii. VWR 61222-548 oven thermometer
   b. Check calibration of all other thermometers and temperature controlling devices against the NIST certified thermometers.

H. Ovens/Refrigerator/Freezers:

1. Daily: When in use.
   Check and record the temperature in all ovens, refrigerators, and freezers.

2. Weekly: Tuesday of each week.
   a. Change temperature recorder paper in Refrigerator #2 and Freezer #4.
   b. Check recorded temperatures for anomalies and report accordingly.

3. Monthly: The last Friday of each month.
   Clean the interior of each oven, refrigerator, and freezer.

4. Semi-Annual: Last Thursday-Friday of January and July
   Defrost BRL Refrigerator #3.

5. Annual: Last Thursday-Friday of January
   Defrost all other refrigerators and freezers as needed.

I. General Lab Cleanliness:

1. Daily:
   Restock shoe cover bins in Hg (Clean Room) and AA Labs.

2. Weekly: Friday of each week.
   a. Wipe all surfaces with a clean, damp rag to remove dust and chemical residues from all lab spaces.
   b. Empty all recycling and garbage bins.

3. Monthly: The last Friday of each month.
   a. Clear, dispose, and store all clutter.
   b. Monitor air for Hg concentration in clean hood of the Hg Lab, by the door of the Hg Lab, and in Receiving and the Prep (Down) Lab.
   c. Wipe inside fume hoods (all walls and benches) located in all labs.

J. Miscellaneous Equipment/Supplies:

1. Pipettes: The calibration must be checked at the user volumes for each pipette prior to use. Monthly, all pipettes must be calibrated over the range of volumes for which they are used.

2. pH Meter:. A two-point calibration should be performed prior to use and the pH meter must be cleaned after each use.

3. Spectrophotometer: The sample compartment and windows must be cleaned prior to and after each use. Lamp alignment and instrument electronics should be checked annually.

4. Laminar Flow Hoods: The prefilters of the flow hoods should be changed quarterly. The Hg removal filters (iodated carbon) should be changed annually, or as needed.

5. Acid Vats: The acid in the vats used to clean bottles and lab ware must be analyzed for mercury concentration at least monthly. Additionally, the temperatures of the vats must be verified monthly.

6. Acids/Reagents: All supplies should be checked weekly and ordered as needed. New acids must be analyzed for Hg concentration prior to use. Reagents used for the analysis of total mercury by EPA Method 1631 must be analyzed for Hg concentration monthly, and when prepared prior to use.

7. Gases: All supplies should be checked weekly and ordered as needed. The air compressor valve must be opened and excess water allowed to drain every other month.

8. Computer Files: All Access and PO databases, QA files, and lab files must be backed-up to CD-ROM on a weekly basis.

4. QUALITY ASSURANCE

A. Monthly Checklist: The QA Manager is responsible for electronically producing a monthly schedule that outlines all of the preventative maintenance required for the upcoming month and specifies who is to complete each task. The schedule contains check-off spaces for each task and room for any necessary comments. Each responsible party is required to enter when they completed each task. At the end of the month, the QA Manager reviews the past month's schedule. Any uncompleted tasks are noted in the QA Managers monthly report and are forwarded to the next month's schedule as necessary.

B. Internal Audits: the QA Manager performs monthly audits of the laboratory spaces and equipment. All equipment logbooks are checked during these audits to ensure that all

equipment performance and maintenance is being properly documented for each instrument.

Exhibit A

Analytical Lab Maintenance Schedule

ITEM	Daily[1]	Weekly	Monthly	Quarterly	Semi-Annual	Annual
Acid Vats			collect & analyze acid for Hg concentration, check temperature			
Balances	calibration check[2]		four-point cal. check[2]			certified calibration[2]
Pipettes	calibration check at set volume(s)		calibrate over range of settings			
Safety Check		flush eyewashes (5) & showers (2)	inspection (CHP app. D)			certify fire extinguishers
Thermometer Calibration			check thermocouplers for wear			check using NIST-certified therm.[2,3]
Temperature Checks	ovens as used, freezer, refrig.[3]	change temp. recorder paper in Ref.#2 & Frz.#4	clean interior of ovens, freezer, refrig.[3]			defrost freezers as needed
Acids/Reagents		check supply, order & test if necessary				
BR-05 CVAFS & MMHg system	rinse/refill DDIW bottle; check fittings; blank traps prior to analysis and after each nonzero	soak bubblers in 1% KOH; blank traps	change loose fittings; prepare new stock standards	condition GC column	replace traps; replace lamp; blank traps on gas lines	clean/change quartz cell; replace GC column
BR-06 CVAFS & T-Hg system	rinse/refill DDIW bottle; check fittings; prepare new pretraps; blank traps prior to analysis	soak bubblers in 1% KOH; blank traps	change loose fittings; prepare new stock standards	replace traps	replace lamp; blank traps on gas lines (replace as needed)	clean/change quartz cell
BR-08 CVAFS & T-Hg system	rinse/refill DDIW bottle; check fittings; prepare new pretraps; blank traps prior to analysis	soak bubblers in 1% KOH; blank traps	change loose fittings; prepare new stock standards	replace traps	replace lamp; blank traps on gas lines (replace as needed)	clean/change quartz cell
Hydride AA (PE 703)	rinse/refill DIW bottle; check fittings; rinse water removal trap	clean spectroph. windows; soak bubblers in 1% KOH	change loose fittings; prepare new stock standards	ensure working traps for As, Se & one backup set	verify backup lamp available; clean nebulizer	fine tune wavelength; check optics; test backup lamps
Hg 245.1 AA (PE 5000)	clean, verify all equip. in working order, check supply of chart paper					

tracking number 02BR001). The samples within a shipment are then each identified by a two digit sequential number. For example, if three samples were received in the 02BR001 shipment they would be given the sample numbers 02BR001-01, 02BR001-02 and 02BR001-03. On the sample receiving log the client's sample ID and the BRL ID numbers are listed for each sample. The BRL tracking numbers (not the client's ID numbers) are referenced during all laboratory preparations and analyses.

Fluoropolymer sample bottles are all engraved with a bottle ID number that is used for sample identification purposes. Clients may wish to use additional sample identification numbers but the unique sample container numbers must be documented on the Sample Receiving Log. When a bottle is removed, the number engraved on the bottle should be matched with the number written on the bag. Any discrepancies should be noted in the Sample Receiving Log. Each bottle should be rinsed with clean DI water (for low-level samples) and/or wiped with a clean cloth. Bottles are then placed in the clean hood, and labeled with the BRL sample number, customer project number, date of sample receipt, client name, and sample preservation information. An example of a BRL sample label is as follows:

02BR450-01 CWP001 4/11/02
City Wastewater Treatment Plant
0.5% BrCl

The original BRL Sample Receiving Log sheets must be signed by the Sample Custodian (or designated alternate) and are kept in a three ring binder at the sample receiving desk. After Sample Receiving Log sheets accumulate up to 100 tracking numbers, the Sample Custodian should bind the originals in a velo-binder and give the bound receiving sheets to the QA Manager for archival.

In addition, an "Internal Custody for Original Samples" form is generated at the time of sample log-in. This form documents the life cycle of each sample shipment from receipt to disposal, and is kept with the samples at all times. After samples have been disposed, the custody forms are stored in the Sample Custodian's files.

8.2.4 Sample Storage

All samples are stored in a secure area. A secure area is defined as a locked area within the premises of BRL with restricted access. To satisfy these custody provisions, the laboratory implements the following procedures:

- Access doors to the laboratory are kept locked, except during normal working hours
- Visitors must sign in and are escorted while in the laboratory
- Samples remain in the secure area until they are removed for sample preparation or analysis

Brooks Rand Ltd. Chain of Custody Record Page____of____

Client:	e-mail address:	Ship to: **Brooks Rand Ltd.**
Contact:	PO #:	3950 6th Avenue NW
Address:	Sampler's signatures:	Seattle, WA 98107
		206.632.6206
		206.632.6017 fax
Phone #:	Client project ID:	e-mail: brl@brooksrand.com
Fax #:	BRL project ID:	www.brooksrand.com

For BRL use only	Cooler temp (°C):	Custody seals present? (Y/N)	Custody seals intact? (Y/N)	Date:	Initials:

	Sample ID	Collection		Miscellaneous				Field Preservation					Analyses required							Comments
		Date	Time	Sampler (initials)	Matrix type	# of containers	Sample field filtered, Y/N	Unpreserved (ice only)	HNO_3	HCl	BrCl	Other (specify)								
1																				
2																				
3																				
4																				
5																				
6																				
7																				
8																				
9																				
10																				

Shipping carrier:			# of coolers:		
Relinquished by:	Date:	Time:	Received by:	Date:	Time:
Relinquished by:	Date:	Time:	Received at BRL:	Date:	Time:

White: LAB COPY Yellow: CUSTOMER COPY

CUSTODY SEAL

Date _____

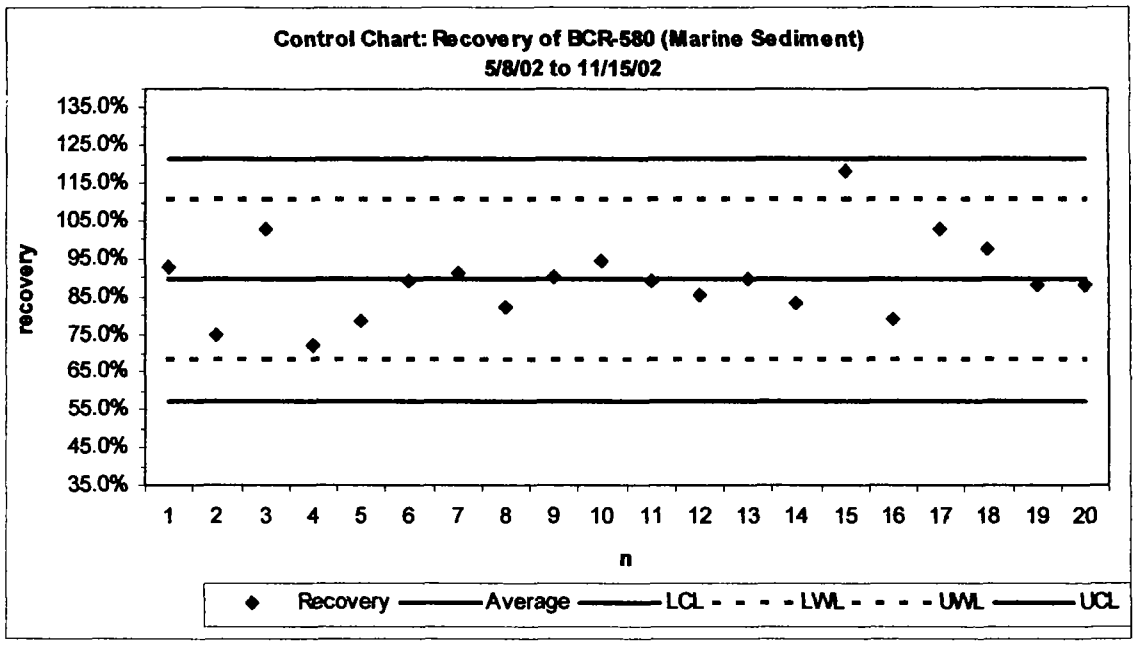
Signature _____

I-CHEM®
Brand Products

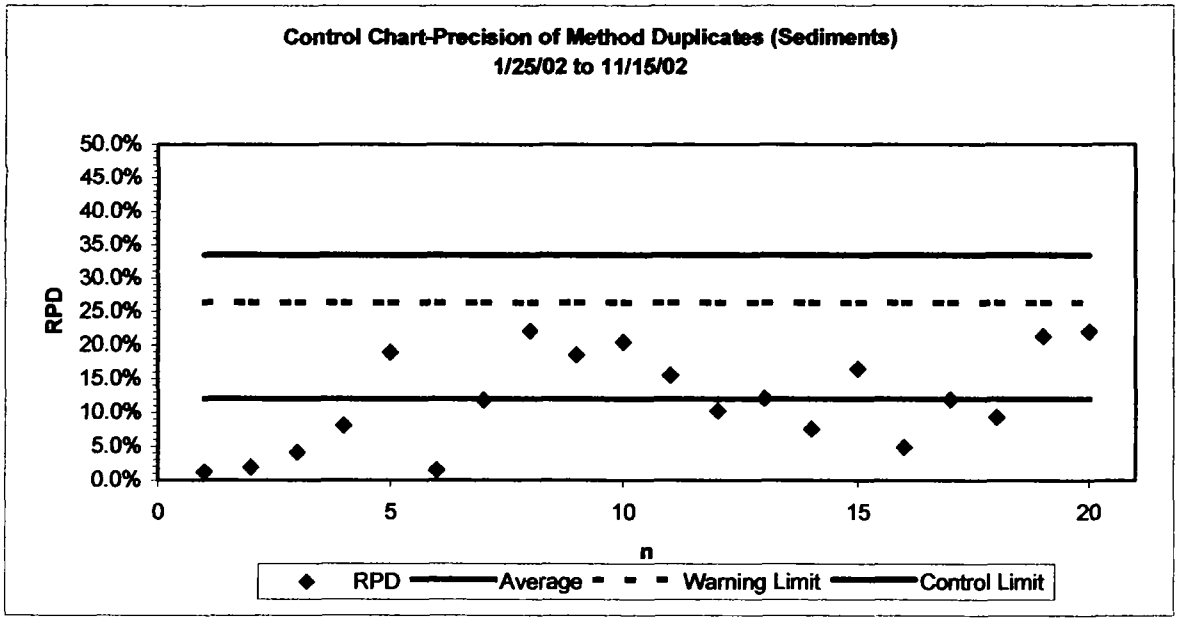
90009

Brooks Rand – Methyl Mercury Control Charts (BR-0011), Sediment/Soil

Accuracy



Precision



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Marine Sciences Laboratory

EFFECTIVE DATE: 9-10-02

Battelle Pacific Northwest National Laboratories
Marine Sciences Laboratory

STANDARD OPERATING PROCEDURE
MSL-I-016-05
TOTAL MERCURY IN TISSUES AND SEDIMENTS BY COLD VAPOR ATOMIC ABSORPTION (CVAA)

Approvals:		
AUTHOR: Brenda Lasorsa	***Original Signature***	9/10/02
	Signature	Date
TECHNICAL REVIEWER: Mary Ann Deuth	***Original Signature***	9/10/02
	Signature	Date
QA OFFICER: Deborah Coffey	***Original Signature***	9-10-02
	Signature	Date
TECHNICAL GROUP MANAGER: Eric Crecelius	***Original Signature***	9-10-02
	Signature	Date

TOTAL MERCURY IN TISSUES AND SEDIMENTS BY COLD VAPOR ATOMIC ABSORPTION (CVAA)

1.0 SCOPE AND APPLICATION

This method is applicable to the determination, in parts per million, of total mercury (Hg) in acid-digested sediment and tissue samples by cold vapor atomic absorption (CVAA). This procedure replaces Battelle procedure, MSL-M-031, and it is a modification of EPA Methods 245.5 and SW-846 7471A. The modification is in the digestion, because the EPA digestions uses potassium permanganate, which is a source of Hg contamination. This method uses the digestion method outlined in the NOAA Technical Memorandum NOS ORCA 130 "Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update". G.G Lauenstein and A.Y. Cantillo, eds.

2.0 SUMMARY OF METHOD

Mercury ions in a digestate are reduced by acidic $SnCl_2$ to Hg^{+}, then carried through a flow cell on a stream of inert gas, i.e. argon. A photometric detector measures the luminous intensity of monochromatic light that has passed through the sample and compares it with the luminous intensity of the same light that has passed through a reference beam. Mercury atoms absorb light at 253.7 nm. The attenuation of the light is directly proportional to the concentration of the mercury vapor, which is quantified using a standard curve. The typical detection limit for the method is 0.001 ug/g.

3.0 RESPONSIBLE STAFF

- Technician - sample digestion
- Analyst- sample analysis
- QA Officer or Representative- data verification

4.0 PROCEDURE

4.1 Sample preparation

Samples shall be digested using an appropriate strong acid digestion, which results in complete sample dissolution. It has been found that the traditional potassium permanganate digestion used in many standard methods for mercury analysis results in unacceptably high and inconsistent blank levels and should be avoided. Digestions done in a closed Teflon® vessel (bomb) are recommended, as many open vessel and microwave techniques result in loss of Hg during venting.

4.2 Apparatus and Reagents

4.2.1 Thermo Separation Products "mercuryModule" (mercury vapor generator).

4.2.2 Thermo Separation Products "mercuryMonitor 3200" (elemental mercury detector).

4.2.3 Thermo Separation Products "autoMetric 3000" (autosampler).

4.2.4 Computer with HgTalk program, screen and printer.

4.2.5 Rinse system for sample siphon - tubing, rinse water bottle, waste water bottle and flow regulating valve.

4.2.6 Acid cleaned (cold 50% HNO_3 for at least 2 days) test tubes, 13 X 100 mm.

4.2.7 Hydrocarbon trap for purifying gas flow into instrument.

4.2.8 Drying trap (4-8 mesh, reagent soda lime is preferred over the magnesium perchlorate that was recommended by the company. The soda lime lasts longer, is less hazardous, and causes less interference).

4.2.9 Pre-pure Argon gas.

4.2.10 Stannous chloride, 10% - add 50 g of $SnCl_2$ to 100 mL low Hg water and 50 mL of HCl in a specially marked Teflon bottle then fill to 500 mL with low Hg water. Bubble nitrogen gas through mixture for at least 6 hours at a very low flow. Transfer solution to 2 specially marked brown bottles. 2% $SnCl_2$ - dilute 50 mL of this 10% $SnCl_2$ with 200 mL of 10% HCl.

4.2.11 Nitric Acid, 3% - add 60 mL of HNO_3 to low Hg water and bring to 2L volume.

4.2.12 Mercury stock standard, 1000 mg/L - purchased from High Purity Standards, Inc.; expiration is usually 1 year.

4.2.13 Mercury intermediate standard, 10 mg/L - dilute 1 mL of 1000 mg/L stock standard into 100 mL of 1% HCl and store at room temperature in a Teflon bottle dedicated for use with the intermediate standard. As long as the standard is stored in Teflon, the standard will be stable for a period of at least 3 months and expiration can be expected to be the same as the stock standard.

4.2.14 Mercury working standards, dilute the intermediate standard (10 mg/L Hg) into 5 concentrations (i.e. 0.5 ug/L, 1.25 ug/L, 5.0 ug/L, 7.5 ug/L and 12.5 ug/L) and store at room temperature in Teflon bottles dedicated for use with standards. As long as the standards are stored in Teflon, the standards will be stable for a period of at least 6 months and expiration can generally be expected to be the same as the stock standard. Check the standards against the certified reference materials (CRMs) run in each analytical batch to verify that the working standards are retaining their titre.

4.3 Interferences

4.3.1 Take appropriate precautions to prevent stannous chloride contamination during sample handling or of any equipment associated with this analysis. If contamination should occur, mercury will be volatilized and lost.

4.3.2 Particle size in samples must be less than 10 µm.

4.3.3 Samples must be totally digested or organic material will interfere with detection.

4.4 Analysis

This analysis is entirely computer based. Software use and troubleshooting will not be reiterated in this procedure, because this information can be found in the software manual.

4.4.1 Allow the mercury monitor at least one hour to warm up before analysis. Turn on the mercury generator, the printer and especially the autosampler before the HgTalk program is loaded or the connection will not be made.

4.4.2 Change the soda lime trap after approximately 100 samples or if the analyzer has not been run for several days. Check the reagent bottles for proper amounts, empty the hazardous waste bottle and the rinse waste bottle, then turn on the argon gas to a pressure of 80 psi. Make sure the reagent pressure gauge reads 5.0 ±1 psi (regulator is on the rear panel) and the flow meter reads about 0.2.

4.4.3 Open HgTalk. There are 3 files necessary for analysis; "method", "sequence", and "data". The method file contains the calibration, integration parameters, and the reports possible. The method file currently being used is called "Hgmeth.hmh". The sequence file is the operation and calculation of the analysis and must be created and named for each analysis set. Each sample has its own data file, which is created during the analysis.

4.4.4 After entering HgTalk and checking that the information in the method file is correct, a sequence file must be created. It is best to have the information organized and calculated before entering the information into the file since this program does not multiply dilution factors or allow the creation of new columns. With the 5 ml loop in the mercury generator, there should be at least 6 ml of sample in the test tube, which does not hold more than 9 ml. The sample can be straight digestate, however this usually does not leave enough digestate for another analysis. 3 mL of digestate and 3 ml of 3% HNO_3 or 1 mL of digestate and 5 mL of 3% HNO_3 are the common dilutions used currently. With the information of sample, weight, and volume times dilution factor ready (see attachment #1 for an example), the new sequence can now be created.

A. Open "edit sequence" and choose "new".
B. Fill in "sequence header" with method file name, create new data file name, operator name and date.
C. Choose "edit", "create entries", answer "yes" to function overwrite, and fill in number of standards and samples.

D. Fill in the sequence spreadsheet that appears with requested information. See Attachment #2 for an example.
E. Choose "SaveAS" and name file. Exit.
F. In the first 6 sample tubes, place a calibration blank and each of the five working standards. These samples will be used to generate the calibration.
G. Pipette the correct volume of 3% HNO_3 into clean test tubes and add appropriate amount of digestate to achieve the desired dilution. Rinse pipette tip several times in the resulting solution. Be sure to pour the correct standard into the vials numbered in the sequence file. Check that the sample vials match the vial numbers in the sequence. Place the tray on the autosampler and check the flow of the rinse water.
H. Load file and choose "run", then "start".

4.4.5 After each calibration standard has been run and the instrument has calculated the calibration curve, verify that the calibration is linear to an r^2 of >0.995. All points on the calibration line must fall within 15% of the line, with the exception of the lowest point, which must not deviate from the line by more than 25%. If these criteria are not met, abort the run and re-run the calibration. If the calibration continues to fail, remake the working standards, repeat the calibration, and continue.

4.4.6 If the absorbance of the sample is higher than the highest calibration standard, reduce the volume appropriately to not less than 5 µL. If the absorbance is still higher than the highest calibration standard, dilute the digestate in a larger acid cleaned vial. If the absorbance of most of the samples in the batch exceeds the highest calibration point, the calibration may be extended by running a higher calibration standard. The analyzer is linear to the range of a 50 µg/L standard. If the result of the 50 µg/L standard is within 10% of the original calibration, the system may be considered linear in that range and the data may be calculated using the original calibration.

4.4.7 Clean the analyzer by running 2-4 samples of 3% HNO_3, then deionized water (DI H_2O) through the machine at the end of each day.

4.5 Instrument Maintenance

4.5.1 The instrument is maintained by the analyst, with the assistance of service personnel at Thermo-Separation Products.

The following items are checked daily and changed weekly (under constant use):

- soda lime
- reagents (stannous chloride, 3% HNO_3, and rinse water)

The following items are checked weekly and changed bimonthly (under constant use):

- carbon trap
- filters

The following items are checked weekly and changed as needed:

- sample injection syringe
- tubing
- connectors
- lamp

4.5.2 The autosampler arm should be cleaned and lubricated bimonthly.

5.0 DATA ANALYSIS AND CALCULATIONS

5.1 The computer program calculates the concentration of Hg in the sample from either peak height or area, which is determined in the method file, by the following equations:

$$[Hg] = ((Ph_s * RF_1) + Rf_0) * V_d / W_d / 0.001 * DF$$

where

[Hg] = Mercury concentration (µg/g dry wt)
Ph_s = Sample peak height or peak area
RF_1 = Response Factor 1 (slope of the regression line in µg/area or height)
Rf_0 = Response Factor (y-intercept)
V_d = Digested volume (mL)
W_d = Digested weight (g)
DF = Dilution Factor

5.2 Data Generation, Review, and Archiving and Software Maintenance

5.2.1 Instrument-generated data are checked using Excel software. All data points are recalculated from the raw peak area and compared to the instrument-generated value. The final data report is rechecked by the QA Officer during the data verification process.

5.2.2 Software is maintained by the analyst with the help of service personnel at Thermo-Separation Products. Backup instrument software is maintained on diskette. Data reduction is done using Excel software purchased and maintained under Battelle's software licensing agreement. Backup copies of all data are maintained on the mercury lab's shared drive, the m-drive.

5.2.3 Electronic data are backed up monthly and also maintained on the analyzer for 1 year. Electronic copies of the data summaries are maintained on the m-drive for two years and then either deleted, forwarded to the client, or archived on diskette as required by the client. Hard copies of all data are maintained in the central file system for at least 10 years.

6.0 QUALITY CONTROL

6.1 One method blank, a sample duplicate, and matrix spike (on a representative sample, to check for matrix interference) should be analyzed per batch of samples or as specified by the customer. A method blank consists of all reagents used in the digestion procedure and it is digested and analyzed as a sample.

6.2 One standard reference material (SRM) should be digested and analyzed with each batch of samples or as specified by the customer, following step 4.4.4.

6.3 An initial calibration verification and continuing calibration verifications should be run every ten samples and must be within 15% of the original calibration. If this check fails, run a duplicate and if that fails rerun the calibration curve and all samples analyzed after the last passing calibration check.

6.4 Data quality objectives, acceptance limits, and corrective actions are outlined in the Table 1 below.

6.5 Method Detection Limits (MDLs) for total mercury are determined by two methods:

6.5.1 To determine general matrix specific MDLs: Analyze 7 replicates of a low level sample (clean sand for sediment or phytoplankton for tissue). Take the standard deviation$_{(n-1)}$ of the 7 replicates and multiply it by the Student's T-value for 7 replicates$_{(n-1)}$ as outlined in MSL-Q-007.

6.5.2 In cases when an empirically derived MDL is not practical (when a clean enough sample can not be found to produce a meaningful MDL for a specific matrix), a theoretical MDL may be calculated. To determine a theoretical sample-specific MDL: Analyze 7 replicates of a low-level liquid standard (0.5 µg/L). Take the standard deviation$_{(n-1)}$ of the 7 replicates and multiply it by the Student's T-value for 7 replicates$_{(n-1)}$ to derive an instrument detection limit (IDL). Put the IDL through the sample concentration calculation (divide by volume analyzed and then multiply by total sample volume and divide by total sample mass).

Battelle MSL does not routinely employ reporting limits (RL). It is MSL policy to report all values detected above the empirically determined MDL (or calculated MDL in the case of tissues or sediments when no empirical MDL can realistically be determined). If a client specifically requests that data be reported below the MDL, the affected data should be flagged as detected below the detection limit according to the client's requested flagging convention.

Table 1. Data Quality Objectives

QC Sample Type	Frequency	Acceptance Limit	Corrective Action
Laboratory Method Blank	1 per batch of 20 or fewer	<5 times the MDL	Reanalyze. If confirmed and all samples are >10 times the blank, no corrective action is required. If samples are <10 times the blank, the batch must be redigested.
Replicate Precision	1 per batch of 20 or fewer	25% for analytes >3 times the MDL No more than 35% of all RSDs can be > 25%[c]	Reanalyze. Failure to meet criteria shall be reported in Data Summary. Failure of multiple DQO's requires redigestion and reanalysis of batch.
Certified Reference Material (CRM) or Standard Reference Material (SRM)	1 per batch of 20 or fewer	75-125% of certified value	Reanalyze. Failure to meet criteria shall be reported in Data Summary. Failure of multiple DQOs requires redigestion and reanalysis of batch.
Matrix Spike (MS)	1 per batch of 20 or fewer	75-125% recovery	Reanalyze. Failure to meet criteria shall be reported in Data Summary. Failure of multiple DQOs requires redigestion and reanalysis of batch.
Initial and Continuing Calibration Verification	every 10 samples	<10% of initial calibration	Reanalyze. If subsequent ICV or CCV still fails, rerun the calibration curve and all samples analyzed after the last passing calibration check.

7.0 SAFETY

All analysts following this procedure should be aware of routine laboratory safety concerns, including the following:

- Protective clothing and eyeglasses should be worn when appropriate.
- Proper care must be exercised when handling samples.

8.0 TRAINING REQUIREMENTS

All staff performing total mercury in tissues and sediments must first read this procedure and then demonstrate proficiency in the process prior to performing any project work. Proficiency may be demonstrated and documented through successful analysis of certified reference materials, performance evaluation (PE) samples, or matrix spike/matrix spike duplicates. Documentation of training will be recorded on a training form obtained from MSL-A-006, Marine Sciences Laboratory Training.

9.0 REFERENCES

Thermo Separation Products HgTalk Mercury Analysis Software

Thermo Separation Products Operator's Manuals for Mercury Vapor Generator and Detector

MSL-A-006, Marine Sciences Laboratory Training.

ATTACHMENT 1
Example Spreadsheet

PROJECT ID: Spreadsheet Examples

ANALYSIS: TSP HG ANALYSER
ANALYSIS DATE:
MATRIX: Sediment/Tissue

ANALYST: Deuth
FILE #: ####

VIAL #	FILE #	SAMPLE ID	DIGEST WT g	DIGEST VOL ml	ANALYZ VOL ml	TUBE VOL ml	DILUT FACTOR	CALC VOL ml
1		0						
2		0.5 µg/l						
3		1.25 µg/l						
4		5.0 µg/l						
5		7.50 µg/l						
6		12.50 µg/l						
7		HNO3 Blk						
8		ICV Std #						
9	100Test	Blank	0.250	23.091	3.000	6	2	46.18
10	100Test	LCS 1	0.250	22.768	3.000	6	2	45.54
11	100Test	MESS-2	0.255	22.905	3.000	6	2	45.81
12	100Test	PACS-1	0.200	23.904	0.100	6.1	61	1458.14
13	100Test	1 R1	0.271	22.929	3.000	6	2	45.86
14	100Test	1R2	0.250	22.922	3.000	6	2	45.84
15	100Test	2	0.278	22.866	3.000	6	2	45.73
16	100Test	3	0.247	22.946	1.000	7	7	160.62
17	100Test	4	0.259	23.017	1.000	7	7	161.12
18	100Test	4 MS1	0.268	23.024	0.500	6.5	13	299.31
19	100Test	4 MSD1	0.258	22.942	0.500	6.5	13	298.25
20	100Test	CCV Std #						

ATTACHMENT 2
EXAMPLE SEQUENCE FILE

File Header Edit Global Change Validate

OVR	SDG	Vial #	Vial #	Phase	Type	Level	Amount	Dilu.Fact
1		2/1	0	liquid	blank	0	1	1
2		2/2	0.5 µg/l	liquid	standard	1	1	1
3		2/3	1.25 µg/l	liquid	standard	2	1	1
4		2/4	5.0 µg/l	liquid	standard	3	1	1
5		2/5	7.50 µg/l	liquid	standard	4	1	1
6		2/6	12.50 µg/l	liquid	standard	5	1	1
7		2/7	HNO3 Blk	solid	sample		1	1
8		2/8	ICV Std #	liquid	sample		1	1
9	100Test	2/9	Blank	solid	sample		0.250	46.182
10	100Test	2/10	LCS 1	solid	sample		0.250	45.536
11	100Test	2/11	MESS-2	solid	sample		0.255	45.810
12	100Test	2/12	PACS-1	solid	sample		0.200	1458.144
13	100Test	2/13	1 R1	solid	sample		0.271	45.858
14	100Test	2/14	1R2	solid	sample		0.250	45.844
15	100Test	2/15	2	solid	sample		0.278	45.732
16	100Test	2/16	3	solid	sample		0.247	160.622
17	100Test	2/17	4	solid	sample		0.259	161.119
18	100Test	2/18	4 MS1	solid	sample		0.268	299.312
19	100Test	2/19	4 MSD1	solid	sample		0.258	298.246
20	100Test	2/20	CCV Std #	liquid	sample		1	1

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Marine Sciences Laboratory

EFFECTIVE DATE: 4-25-00

Battelle Pacific Northwest Laboratories
Marine Sciences Laboratory

STANDARD OPERATING PROCEDURE

MSL-A-001-04

SAMPLE LOG-IN PROCEDURE

Approvals:		
AUTHOR: Laurie Niewolny	***Original Signature***	4/24/00
	Signature	Date
TECHNICAL REVIEWER: Carolynn Suslick	***Original Signature***	4/25/00
	Signature	Date
QA OFFICER: Deborah Coffey	***Original Signature***	4-21-00
	Signature	Date
TECHNICAL GROUP MANAGER: Eric Crecelius	***Original Signature***	4-24-00
	Signature	Date

SAMPLE LOG-IN PROCEDURE

1.0 SCOPE AND APPLICATION

This method applies to sample receipt, log-in, preservation, storage, and disposal of all chemistry water, soil, sediment and tissue samples by the Battelle Marine Sciences Laboratory (MSL) Sample Custodian or designee.

2.0 DEFINITIONS

Log-In - The procedure by which samples are received and documented at the (MSL).

Sample Custodian - The person responsible for sample receipt and log-in.

CoC Form - Chain-of-custody form, accompanies samples from field to MSL and is kept with the sample files.

3.0 RESPONSIBLE STAFF

Sample Custodian or designee
Project Manager
Data Coordinator
Quality Assurance Officer or Representative

4.0 PROCEDURE

4.1 Sample Receipt

4.1.1 Samples arrive from the customer via a variety of delivery systems (e.g., United Parcel Service, Federal Express, Air Borne, Courier Service, General Delivery or from staff within MSL). The Sample Custodian is notified of sample arrival by either the shipping clerk or directly by the MSL staff member who has custody of the samples. The Log-In Checklist (see Attachment 1) is initiated.

4.2 Sample Log-In

4.2.1 The shipping container is inspected for a custody seal and opened. The container temperature is taken immediately and recorded on the Log-In Checklist. A calibrated thermometer or temperature probe (see MSL-W-003, Calibration and Use of Thermometers, for calibration instructions) is placed in the cooler in a representative location (not

directly touching any ice or cold packs). If a temperature blank sample is provided, this should be used to measure the container temperature at the time of receipt. Acceptable shipping temperatures are less than or equal to room temperature for metals in preserved water samples. For unpreserved water, tissue, sediment, or soil samples, container temperature(s) should be 4°C $\pm$ 2°C; however, solid samples (tissue, sediment, and soil) can be frozen.

4.2.2 Individual samples are then removed from the shipping container and inspected for the presence of sample custody seals, the intactness of the seals, damage, leakage, missing labels and/or other problems. These problems are noted on the Log-In Checklist. The sample identification numbers are compared to the CoC form that accompanies the samples to ascertain whether all samples are present and whether or not the labels on the containers match those on the CoC form. If no CoC form accompanies the samples, a MSL CoC form will be initiated and filled in with the sponsor codes listed on the sample labels.

4.2.3 At this point, the Project Manager should be notified of the number and condition of the samples (i.e., if any seals have been broken, sample containers are damaged, and/or the cooler temperature(s) are out of limits). The project manager is responsible for contacting the customer regarding problems that may affect the integrity of the samples or subsequent analyses. The discrepancy, its resolution, and the identity of the person contacted must be documented in the project file.

4.2.4 After complete inspection of the samples, the "Received By" section of the CoC form must be signed and dated, along with the receipt time, by the Sample Custodian.

4.2.5 From the Project Log-In/Central File Index (Log-In book), a project or initial set of samples is assigned a sequential central file number (CF#). The log-in book is a spiral notebook in MSL-5, Room 130. Subsequent sample sets received for ongoing projects are logged in with the same central file number. A group of samples can be one of several things: a set of samples from one sampling period or a continuous influx of samples from one project. The project manager usually determines this.

4.2.6 Each sample is then assigned an individual number after the central file number (e.g., 1205*1, 1205*2, etc...). Samples from an ongoing project are numbered beginning with the last number assigned. This number is called the MSL sample ID, and is recorded on the CoC form and on the corresponding sample container. All samples are referred

to by the MSL sample ID from this point on until the data are reported, when the sponsor ID is matched back to the MSL sample ID.

4.2.7 The Sample Custodian records in the log-in book (see Attachment 2) the central file number, date samples are received, file name, project sample description, samples numbers, storage location and the custodian's initials.

4.3 *Sample Filtration, Preservation and Storage*

4.3.1 Samples are appropriately preserved to ensure sample holding times, depending on the matrix and analyses. In addition, container type and amount of sample are observed to make sure the integrity of the sample is maintained. Tables 1 and 2 provide recommended practices for sample preservation and container types. If there are any deviations, the deviation shall be documented and the Project Manager should be notified for direction.

Table 1. Preservation Recommendations

Analysis Requested	EPA 1600 Series and EPA 245 Suggested Practices	MSL Recommended Practices	Holding Time
Metals in water - except methyl Hg, Cr^{3+}, and Cr^{6+}	Acidify with ultrapure nitric acid to pH<2 (0.2%)	2mL concentrated ultrapure nitric acid/1L sample (0.2%) to pH<2	6 months
Total Hg in water	Acidify to 0.5% with ultrapure HCL or BrCl to pH<2 (0.5%)	5mL concentrated ultrapure HCl/1L sample (0.5%)	28 days
Methyl Hg in water	4 mL concentrated ultrapure HCl/1L freshwater sample or2mL concentrated sulfuric acid/1L seawater sample	5 mL concentrated ultrapure HCl/1L freshwater sample or 5mL 8M sulfuric acid/1L seawater sample	28 days
Cr^{3+} water samples	Add 1mL Cr^{3+} extraction solution to 100mL sample, vacuum filter through 0.4µm membrane, add 1mL concentrated ultrapure nitric acid to filter	Add 1mL Cr^{3+} extraction solution to 100mL sample, vacuum filter through 0.4µm membrane, add 1mL concentrated ultrapure nitric acid to filter	6 months
Cr^{6+} water samples	1mL 50% NaOH /125mL sample and refrigerate	1mL 50% NaOH /125mL sample and refrigerate	30 days
Arsenic speciation in water	Acidify pH<2 with HCl and refrigerate	2mL concentrated ultrapure HCL/1L sample (0.2%) and refrigerate	28 days

Table 1. Preservation Recommendations (continued)

Analysis Requested	EPA 1600 Series and EPA 245 Suggested Practices	MSL Recommended Practices	Holding Time
Selenium speciation in water	Not applicable	2mL concentrated ultrapure HCL/1L sample (0.2%) and refrigerate	28 days
Metals in tissue, sediment, and soil	Ship cold (4°C ±2°C) then freeze dry	Freeze and/or refrigerate (4°C ± 2°C) then freeze dry	6 months
Total Hg in tissue, sediment, and soil	Ship cold (4°C ±2°C) then freeze dry	Freeze and/or refrigerate (4°C ± 2°C) then freeze dry	28 days
Methyl Hg in tissue	Ship cold (4°C ±2°C) then freeze dry	Freeze and/or refrigerate (4°C ± 2°C) then freeze dry	28 days
Methyl Hg in sediment	Ship cold (4°C ±2°C) DO NOT FREEZE DRY	Freeze and/or refrigerate (4°C ± 2°C) DO NOT FREEZE DRY	28 days

Table 2. Container Types and Minimum Samples Amount

Analysis Requested	Container Type	Minimum Required Amount
Metals in water (except mercury)	fluoropolymer (FEP; Teflon™), polyethylene, polycarbonate, or polypropylene bottles with lids	150 mL
Metals in sediment and tissue	glass, polyethylene, polystyrene (SPEX) jars	10-20 g wet
Total and methyl Hg in water	fluoropolymer (FEP; Teflon™) or glass bottles with fluoropolymer or fluoropolymer-lined lids	500 mL
Total and methyl Hg in sediment and tissue	fluoropolymer (FEP; Teflon™), glass, or polystyrene (SPEX) jars	10-20 g wet

4.3.2 If water samples arrive unpreserved, the project manager is consulted to determine if filtration or preservation is required. Sample pH may be randomly measured to assure that samples are not preserved when other information is unavailable. Water samples have to be filtered before preservation with acid. Once filtration is complete, samples are acidified and all is noted on the Log-In Checklist form.

If the samples are to be analyzed for the Navy and are water samples for metals or mercury (Hg) analysis, the pH (see MSL-W-001, Calibration and Use of pH Meters) for all samples will be measured and the result and time of measurement documented using the form found in MSL-I-028, Navy Sample Analyses Plan. The pH of all other water samples for metals will be determined based on customer request.

4.3.3 Tissue, sediment and soil samples can be held in a refrigerator or freezer until sample preparation. If samples require freeze drying as per Project Manager instructions, samples are weighed and placed in the ultra-low temperature freezer (-68 ± 5°C) located in MSL 5, Room 130.

4.3.4 All samples are placed in the location specified in the sample log-in book by the sample custodian. At this time, the Log-In Checklist is completed, signed and dated by the Sample Custodian.

4.3.5 Additional project information must be obtained from the project manager prior to the electronic log-in of the samples. This includes the customer name and sample analyses required. At this point, the sample information will be used to generate a computer spreadsheet of the sample log-in information called the Sample Log-In spreadsheet (see Attachment 3). A copy of the Sample Log-In form along with the completed Chain-of-Custody form(s), Log-In Checklist, and any custody information that accompanied the samples should be given to the Project Manager accompanied by a kit/addendum (see MSL-D-004, Data Reporting, Reduction, Back Up, and Archiving). The Project Manager will complete the kit/addendum and forward the packet to the Data Coordinator. The Data Coordinator will disperse copies of the kit/addendum to the appropriate analysts.

4.4 Sample Disposal

Sample disposition can either consist of returning samples to the customer or disposing of samples into an appropriate waste receptacle. Sample disposition requirements are documented on the Log-In Checklist. MSL sample disposition is mandated by the formal, Battelle Pacific Northwest National Laboratory-controlled document issued under the Standards Based Management System (SBMS) in the subject area of "Chemical Management System". The SBMS is a web-based policy and procedures resource for Battelle staff, which guides day-to-day operations. The Chemical Management System (CMS) tracks solution disposal (e.g., for samples, reagents, standards, etc.) Samples are labeled as to their disposition date when archived. A Sample Disposal Logbook is used to document Sample Disposal.

5.0 DATA ANALYSIS AND CALCULATION

Not applicable to this procedure

6.0 QUALITY CONTROL

The Project Manager reviews the CoC and Log-In Checklist for correctness and completeness before the kit/addendum is completed. When the QA reviews the data, the CoC and Log-In Checklist are reviewed again for correctness and completeness.

7.0 SAFETY

Precautions should be used when handling samples. Gloves, safety glasses and laboratory coats should be worn when handling samples of unknown content.

8.0 TRAINING REQUIREMENTS

Appropriate health & safety training is required to handle hazardous samples. All staff members who will be designated as a Sample Custodian shall first read this procedure. Documentation of training will be recorded on a training assignment form from MSL-A-006, Marine Sciences Laboratory Training.

9.0 REFERENCES

MSL-W-003	Calibration and Use of Thermometers
MSL-W-001	Calibration and Use of pH Meters
MSL-I-028	Navy Sample Analyses Plan
MSL-D-004	Data Reporting, Reduction, Back Up, and Archiving
MSL-A-006	Marine Sciences Laboratory Training

Attachment 1
Example Log-In Checklist

LOG-IN CHECKLIST Reference SOP# MSL-A-001

Central File #: _____ Project Manager: _____

[redacted]

Matrix: _____ WP# _____

Yes	No	
☐	☐	Navy-type Project (requires high-level sample tracking procedures)
☐	☐	Filter Samples: [redacted]
☐	☐	Freeze dry sample(s) - samples will be weighed and placed in Ultra-low temp freezer (Lab# 130)
☐	☐	Special instructions: _____

Sample Preservation Instructions: _____

Date To Archive: _____ Date To Dispose: _____

TO BE COMPLETED UPON SAMPLE ARRIVAL/LOG-IN

Yes	No	N/A	Initial Appropriate Box When Completed	
☐	☐	☐	Custody seal present	
☐	☐	☐	Custody seal intact	
☐	☐	☐	Cooler(s) temperature (acceptable range 4°C±2°)	_____ °C
			(if multiple coolers, note temp. of each)	_____ °C
☐	☐	☐	Project Manager notified of any discrepancies or if temperature outside acceptable range? Comments/Remedy: _____	
☐	☐	☐	All chain of custody forms signed and dated?	
☐	☐	☐	Samples Filtered?	

Sample condition(s): [redacted]

Container type: [redacted]

Notes: _____

Completed By: _____ Date/Time: _____

Attachment 1
Example Log-In Checklist (continued)

SAMPLE PRESERVATION

☐ Sample preserved upon arrival at MSL (noted on CoC / Sample / per PM Instruction)

☐ Random pH checked for ~10% of samples (use dip paper) Sample IDs: _____

☐ Complete pH check required for project (use pH meter and record on pH Record form)

If preservation necessary, record Acid Lot#

Type: ☐ 0.2% HNO3 Notes: _____

☐ 0.5% HCl (Hg samples) Notes: _____

☐ Refrigerate Notes: _____

☐ Freeze Notes: _____

☐ Other Notes: _____

Completed By: _____ **Date/Time:** _____

Attachment 2
Example Project Log-In/Central File Index (Log-In Book)

DATE	INITIALS	FILE NAME	PROJECT	SAMPLE DESCRIPTION	# OF SAMPLES	STORAGE LOCATION

Attachment 3
Example Sample Log-In Spreadsheet

cc: PM/CF Log-In File	**Project Title:**	**Example Sample Log-In Sheet**			**Project Manager:** **Date Received:**	
SPONSORR CODE	Battelle MSL Sample ID	Matrix	Storage Location	Parameters requested	**Collection Date**	Initials
Dump Site 1	***1205*1***	***Sediment***	***Hg Lab***	*MeHg*	***02/29/99***	***LN***

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Marine Sciences Laboratory EFFECTIVE DATE: 4-10-02

Battelle Pacific Northwest National Laboratories
Marine Sciences Laboratory

STANDARD OPERATING PROCEDURE
MSL-A-002-03

SAMPLE CHAIN-OF-CUSTODY

Approvals:		
AUTHOR: Deborah Coffey	***Original Signature***	4-10-02
	Signature	Date
TECHNICAL REVIEWER: Carolynn Suslick	***Original Signature***	4-10-02
	Signature	Date
QA OFFICER: Deborah Coffey	***Original Signature***	4-10-02
	Signature	Date
TECHNICAL GROUP MANAGER: Eric Crecelius	***Original Signature***	4-10-02
	Signature	Date

SAMPLE CHAIN-OF-CUSTODY

1.0 SCOPE AND APPLICATION

This procedure defines the methods for establishing the traceability of samples transferred to the Battelle Marine Science Laboratory (MSL) for chemical and/or biological testing. This process ensures the integrity of the samples from the time of collection through sample disposal. The sequential custody of samples will be documented using this procedure. Each custodian of the samples shall comply with the procedures described below.

2.0 DEFINITIONS

- **Custody** - Having control of the sample in one or more of the following manners: 1) physical possession; 2) in person's view after taking possession; 3) secured by a person in a manner that prevents tampering of sample; and/or 4) secured by a person in an area restricted to authorized personnel.
- **Sample Custodian** - The person assigned, at a given field site, laboratory, or testing facility, for having responsibility for custody of the sample.
- **LRB** - Laboratory Record Book
- **CoC** – Chain of Custody

3.0 RESPONSIBLE STAFF

Marine Sciences Laboratory (MSL) Staff as Sample Custodian or as Sample Recipient or as MSL Contact -
Project Manager or Task Leader
MSL Manager
MSL Quality Assurance Officer or Representative

4.0 PROCEDURE

4.1 Custody Procedures in the Field or Laboratory

4.1.1 The sample custodian may be a member of the sampling crew or a person that works with those who are collecting the samples. The sample custodian ensures that sample labels are filled out and affixed to the appropriate sample containers before or at the time of sample collection.

Information on the sample labels may include, but not be limited to, a code number identifying the sample, date, time, and location of sample collection, and name of sample collector.

4.1.2 Once the samples are collected, the sample custodian records pertinent sample collection information on required raw data documentation (i.e., sample log, LRB, etc.). Information may include, but not be limited to, a code number identifying the sample, date, time, and location of sample collection, and name of sample collector.

Record in permanent ink all pertinent information about each sample on a Chain-of-Custody Form (Attachment 1 or 2). Press hard when making entries and assure transfer to carbon copies. Multiple samples collected on the same date may be recorded on one Chain-of-Custody Form, provided each sample is identified individually on the form.

Note: The Field Sample Chain of Custody (Attachment 1) is used primarily when transferring samples from the field to the MSL for processing. The Sample Custody Record (Attachment 2) is used when transferring samples from the field or the MSL to another laboratory or testing facility. For the purpose of this SOP, the term Chain-of-Custody Form can mean either of the two forms.

4.1.3 If required by a project-specific protocol, the sample custodian attaches custody seals to the samples or to the shipping container (e.g., ice chest) immediately on sample collection. The seal is attached in such a way that the sample cannot be opened without breaking the seal.

4.1.4 If there are special storage requirements (i.e., temperature requirements), the sample custodian ensures that samples are immediately stored using the required method and appropriate containers.

4.1.5 The sample custodian is responsible for the samples during delivery to the MSL, laboratory or testing facility until custody of the samples can be transferred to the sample recipient or until release of the samples during shipment (e.g., if samples have to be shipped via overnight carrier, etc.). If custody of the samples cannot be transferred to the sample recipient or shipped on the same day as sample collection, the samples must be stored in a locked or secured storage area until the transfer can be made.

Note: Chain-of-Custody Forms shall remain with samples during transfer.

4.2 Transferring Custody of Samples to a Laboratory or Testing Facility

4.2.1 Upon arrival at the laboratory or testing facility or just prior to releasing samples for shipment, the sample custodian examines the sample container(s) to ensure that the sample seals are intact and the sample containers have not been damaged.

4.2.2 The sample custodian relinquishes custody by signing, dating, and noting the time in the "Relinquished By" space on the Chain-of-Custody Form. The sample custodian tears off the bottom copy (pink) of the Chain-of-Custody Form and retains it for filing with project files.

4.2.3 The sample recipient takes custody of the samples by signing, dating, and noting the time in the "Received By" space on the Chain-of-Custody Form. The sample recipient now becomes the laboratory sample custodian, completing the transfer of sample custody. The contents of the shipping container must be checked against the information on the chain-of-custody form for anomalies. If any discrepancies are noted, or if laboratory acceptance criteria or project-specific criteria are not met, the laboratory must contact the client's designated point of contact for resolution of the problem. The discrepancy, its resolution, and the identity of the person contacted must be documented in the project file. If any seals have been broken and/or the sample containers are damaged, the sample recipient records the condition of the seals and containers in the remarks section of the Chain-of-Custody Form.

4.2.4 The Chain-of-Custody Forms travel with the samples during the transfer, and are filed in the laboratory or testing facility's project files.

4.3 Internal Chain of Custody

MSL does not routinely invoke a formal internal chain of custody process. Access to the building is limited by requiring all staff members to have electronic access cards to enter the building (refer to MSL-A-011, Marine Sciences Laboratory Access Control.) Visitors are issued daily badges. After hours site access is maintained by a gated fence to the grounds and the presence of a security guard. Non-analytical staff are not encouraged to be in areas when they have no reason to be there.

The laboratories are physically located in close proximity to one another and samples are within the physical control of the analysts during digestion and analysis activities. Samples are received in the shipping and receiving area, and logged in per procedure MSL-A-001, Sample Log-In Procedure, and stored until digestion (if required) and analysis. MSL does not store digestate for re-analysis. Instead, if a sample requires re-analysis it is digested from an archived sample. Access to sample archive refrigerators and freezers is restricted.

A Log-in Checklist (see Appendix of MSL-A-001) is used to document sample sample receipt activities, verification of field sample preservation, sample filtration and preservation when required, and to document any deviations related to sample receipt and sample log-in.

MSL documentation provides the location of the sample post-receipt on the Sample Log-In Form. Digestion sheets provide a record of sample digestion dates. Analysis times are documented on raw data print outs. Sample disposition is determined by the client and is documented on the Log-In Checklist in the section completed by the Project Manager. Sample disposition processes are documented in MSL-I-026, Use of Laboratory Refrigerators and Freezers. When an internal chain of custody report is desired, it can be generated from data sheets in the sample analysis data file, and verified against the data file documentation by the Project Manager and MSL QA Officer.

4.4 Evidentiary/Legal Chain of Custody

In a few cases, clients request samples to be tracked under evidentiary/legal chain of custody requirements. In these cases MSL is prepared to establish an intact, continuous record of the physical possession, storage and disposal of sample containers, collected samples, sample aliquots, and sample extracts or digestates, accounting for all time periods associated with sample receipt, processing, analysis and storage and disposal. When evidentiary/legal chain of custody is requested, MSL documents all sample fates in a summary traffic report for the client based on objective evidence maintained during the sample processing. Objective evidence will be defined as all information necessary to produce unequivocal, accurate records that document the laboratory activities associated with sample receipt, preparation, analysis, reporting, archiving, and disposal. Including signatures of all individuals who physical handle individual samples.

When evidentiary/legal chain of custody is required, the assigned project manager will discuss the following requirements with the client to determine which items are required and to ensure that all relevant items are addressed because different programs have different requirements and to assist in project planning.

1. The point at which evidentiary/legal chain of custody is initiated and whose responsibility it will be must be defined.

2. Determine if samples will be shipped in individual sample containers with custody seals intact.

3. Determine if samples will be shipped in coolers with custody seals intact.

4. Determine if the chain of custody forms will remain with the samples during transport or shipment.

5. Determine if the tracking records for legal COC will include the time of day and calendar date of each transfer or handling procedure.

6. Is the expectation that the laboratory will retain the receipts of packages sent by common carrier as a part of the permanent chain-of-custody procedure?

7. Determine if the desired level of evidentiary/legal chain of custody includes the requirements that laboratory personnel: (1) are responsible for the care and custody of the sample and (2) prepared to testify that the sample was in their possession and view or secured in the laboratory at all times from the moment it was received from the custodian until the time that the analyses are completed or the sample is disposed

MSL is not always able to control steps 1-5 above, when MSL is not responsible for sample collection, labeling, preservation, handling, and shipment.

4.5 Subdividing Samples

Once at the MSL laboratory or testing facility, if samples have to be subdivided and submitted to a subcontractor laboratory, this information will be noted on the original Chain-of-Custody Form (from sample collection), and a new Chain-of-Custody Form is initiated. With each transaction, the sample custodian relinquishes custody to the sample recipient, who then becomes the next sample custodian. (See Sections 4.2.2 through 4.2.4 above.) The requirements for chain of custody and sample disposition will be noted on the Chain-of-Custody form.

4.6 Disposal of Samples

4.6.1 When samples are disposed of by the subcontractor laboratory:

- If the subcontractor laboratory or testing facility is responsible for disposing of the samples, the subcontractor is asked to notify the MSL Project Manager before final disposition. The MSL Contact will notify the originator that the samples are scheduled to be destroyed, or will define customer requirements for an extended period of storage.

- After destruction of samples, the subcontractor laboratory or testing facility is asked to return a copy of the Chain-of-Custody Form to the MSL Contact for placement in project files. The originator may be forwarded a copy of the final Chain-of Custody documentation if requested.

- The MSL Contact records the date of receipt on the Chain-of-Custody Form in the "Received by" section of the form space and indicates the samples were destroyed ending the chain of possession.

4.6.2 When samples are disposed of by the Marine Sciences Laboratory (MSL):

- If the laboratory or testing facility is not responsible for disposal of the samples, MSL personnel will obtain custody of the samples from the subcontractor laboratory or testing facility along with the Chain-of-Custody Form.

  For returned samples or samples that have never left MSL custody, the MSL Contact will notify the originator that the samples are scheduled to be destroyed, or will define customer requirements for an extended period of storage.

  If extended storage is not requested, then MSL will dispose of the samples following the guidelines specified in the Pacific Northwest National Laboratory's (PNNL's) Standards-Based Management System (SBMS). This system provides a framework for logging in reagents, chemicals and solutions into the associated Chemical Management System (CMS). This system provides the PNNL Laboratory with the policies and procedures regarding tracking and inventory, storage and disposal of completed samples and analytical wastes, as well as chemical use and disposal. The CMS is used to provide an up-to-date inventory to facilitate emergency response, monitor the location of various classes of materials and identify situations where acceptable limits for the building/facility determined by the assigned chemical hazard group and fire zone might be exceeded before a violation occurs.

- After destruction of samples, MSL personnel responsible for sample destruction returns a copy of the Chain-of-Custody Form to the MSL Contact and the Sample Disposal Log Book entry is updated.

- The MSL Contact records the date of receipt on the Chain-of-Custody Form in the "Received by" space next to the Sample Custodian's signature and indicates the samples were destroyed ending the chain of possession.

4.6.3 When samples are returned to the customer for disposal:

- Samples may be returned to the customer (or the sampling site) by customer request. Samples are shipped to meet Department of Transportation regulations Generally, the samples are shipped in the same way that they were initially shipped to MSL. Sample disposition should be documented in the central file of each project.

4.5.4 The MSL Contact shall ensure that completed Chain-of-Custody Forms are

filed in the appropriate project files. The originator may be forwarded a copy of the final Chain-of Custody documentation if requested.

5.0 DATA ANALYSIS AND CALCULATIONS

There are no calculations applicable to this procedure.

6.0 QUALITY CONTROL

It is the responsibility of each individual taking or relinquishing custody of the samples to ensure that Chain-of-Custody Forms are filled out accurately and completely for each transaction, and that the forms are filed in the appropriate project files.

If the Chain of Custody is broken at any time when the sample is in the control of MSL, this deviation must be documented in the data report narrative.

7.0 SAFETY

Not applicable.

8.0 TRAINING REQUIREMENTS

All staff responsible for sample custody (i.e., sample relinquisher or sample recipient) shall first read this procedure and document the training as a completed reading assignment on an Individual Training Assignment Form or a Group Training Documentation Form as described in MSL-A-006, Marine Sciences Laboratory Training.

9.0 REFERENCES

MSL-A-001	Sample Log-In Procedure
MSL-A-006	Marine Sciences Laboratory Training
MSL-A-011	Marine Sciences Laboratory Access Control
MSL-D-004	Data Reporting, Reduction, Back Up, and Archiving
MSL-I-026	Use of Laboratory Refrigerators and Freezer

Attachment 1

Battelle Marine Sciences Laboratory 1529 W. Sequim Bay Rd. Sequim, WA 98382	**EXAMPLE** **FIELD SAMPLING CHAIN OF CUSTODY**	Page ____ of ____

Shipped To:

Method of Shipment:

Shipped From: By:

Company: Telephone:

Address:

SPECIAL INSTRUCTIONS:

Container No.:

Sampling Location:

Samples Collected By: Date:

Remarks:

SAMPLE IDENTIFCATION	

Relinquished by	Date/Time	Received by	Date/Time
Relinquished by	Date/Time	Received by	Date/Time
Relinquished by	Date/Time	Received by	Date/Time

ATTACHMENT 2

EXAMPLE
SAMPLE CUSTODY RECORD Date _____
Page of

Battelle
Marine Sciences Laboratory
1529 West Sequim Bay Road
Sequim, Washington 98362

Project No.:				Testing Parameters							Laboratory:
Project Name:											Address:
Project Manager:											
Phone:											Attn:
										Number of Containers	
Lab No.	Sample No.	Collection Date	Matrix								Observations, Instructions
											total # of containers

Relinquished by:	Received by:	Shipment Method:
Signature Date Time	Signature Date Time	Special Requirements or Conditions:
Printed Name Company	Printed Name Company	Sample Disposition:
Relinquished by:	Received by:	Distribution:
Signature Date Time	Signature Date Time	1. 2 copies to the Laboratory 2. 1 copy project manager 3. Return completed original to Battelle Marine Sciences Laboratory
Printed Name Company	Printed Name Company	

SAMPLE CUSTODY RECORD

(SOP# MSL-A-001 & MSL-A-002)

Date: _____

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Pacific Northwest Division
Marine Sciences Laboratory
1529 West Sequim Bay Road
Sequim, Washington 98382

Project Name: _____
Project Manager: _____
Phone Number: _____

Shipment Method: _____
Preservation: _____

Line	Field Sample ID	Collection Date/Time	Matrix	No. of Containers	Test Parameters					Laboratory ID	Observations/Comments
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											

Relinquished By:	Company:	Received By:	Company:
Signature/Printed Name	Date/Time	Signature/Printed Name	Date/Time
Relinquished By:	Company:	Received By:	Company:
Signature/Printed Name	Date/Time	Signature/Printed Name	Date/Time

Rev. 020102COC

Distribution: White - Laboratory, Project Files Yellow - Laboratory, Client Pink - Sampler

Page _____ of _____

Weatherproof Laser Labels

Use template for 5164™

Battelle Marine Science Laboratory
Container Specially Cleaned for Trace Metals
Date:

Sample ID:	**Date:**
Lab ID:	**Time:**
Site Description:	**Collected by:**
Parameters:	**Preservative:**

Battelle Marine Science Laboratory
Container Specially Cleaned for Trace Metals
Date:

Sample ID:	**Date:**
Lab ID:	**Time:**
Site Description:	**Collected by:**
Parameters:	**Preservative:**

Battelle Marine Science Laboratory
Container Specially Cleaned for Trace Metals
Date:

Sample ID:	**Date:**
Lab ID:	**Time:**
Site Description:	**Collected by:**
Parameters:	**Preservative:**

Battelle Marine Science Laboratory
Container Specially Cleaned for Trace Metals
Date:

Sample ID:	**Date:**
Lab ID:	**Time:**
Site Description:	**Collected by:**
Parameters:	**Preservative:**

Battelle Marine Science Laboratory
Container Specially Cleaned for Trace Metals
Date:

Sample ID:	**Date:**
Lab ID:	**Time:**
Site Description:	**Collected by:**
Parameters:	**Preservative:**

Battelle Marine Science Laboratory
Container Specially Cleaned for Trace Metals
Date:

Sample ID:	**Date:**
Lab ID:	**Time:**
Site Description:	**Collected by:**
Parameters:	**Preservative:**

Revision to the QA/SAPP

Figure 3

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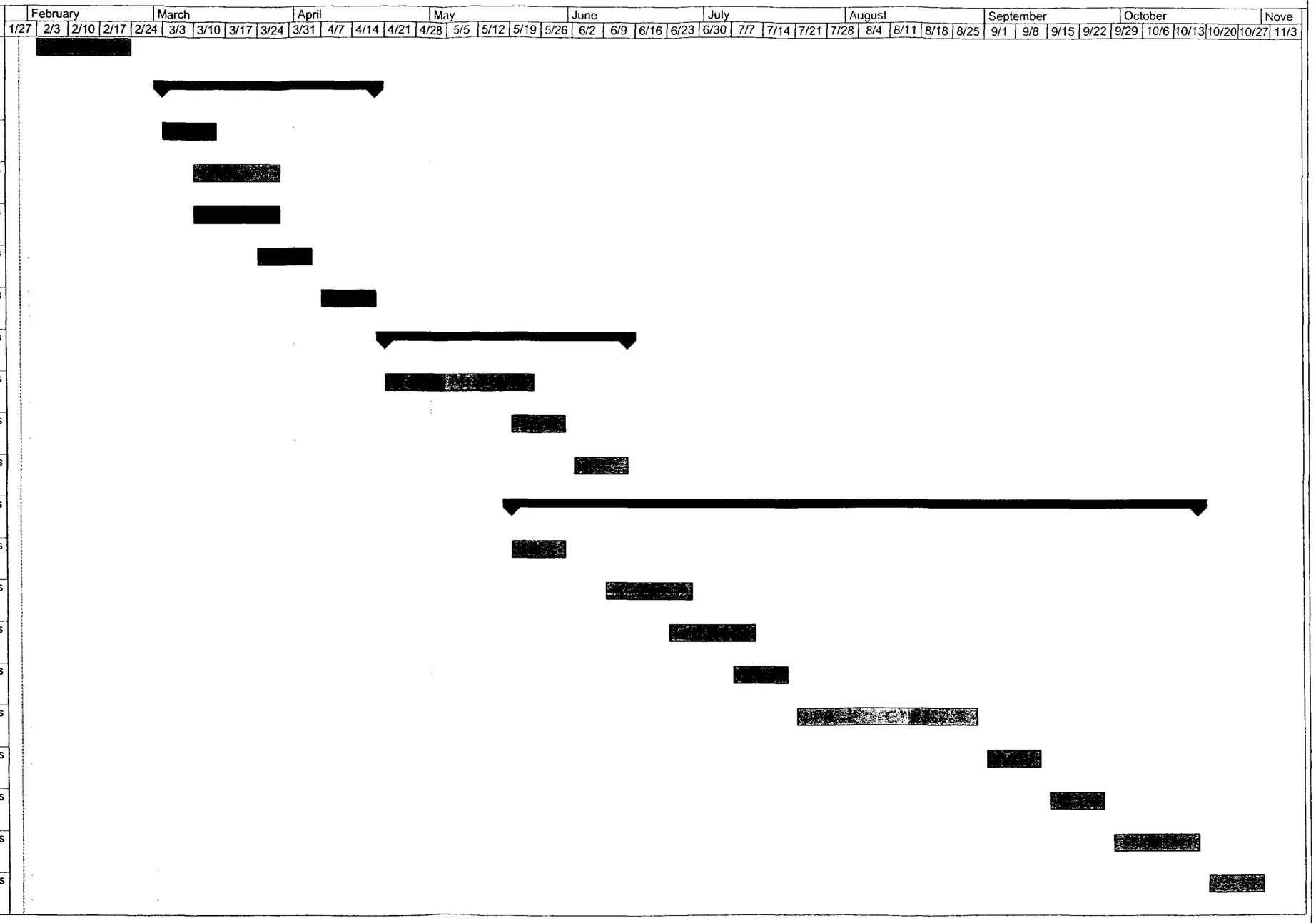
engineers & scientists

FIGURE 3. PROJECT TIMELINE

ID	Task Name	Duration
1	EPA APPROVAL OF QAPP	15 days
2	**FIELD WORK**	**35 days**
3	Sample Location Survey	10 days
4	Sediment Characterization	15 days
5	Sediment Sampling	15 days
6	Field Reporting	10 days
7	Data Review and Validation	10 days
8	**LABORATORY ANALYSIS**	**40 days**
9	Laboratory Analysis	25 days
10	Data Review and Validation	10 days
11	Data Evaluation	10 days
12	**REPORTING**	**110 days**
13	Data Validation Report	10 days
14	Draft Sediment Report Preparation	15 days
15	Internal Review of Draft Report	15 days
16	Submittal of Draft Report to EPA	10 days
17	EPA Review of Draft Report	30 days
18	Draft Report Revisions	10 days
19	Draft Final Re-Submittal to EPA	10 days
20	EPA Review of Draft Final	15 days
21	EPA APPROVAL OF REPORT	10 days



Project: Project Timeline
Date: Thu 1/30/03

Task | Progress | Summary | External Tasks | Deadline
Split | Milestone | Project Summary | External Milestone

Revision to the QA/SAPP

Section 4

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4. Quality Objectives and Criteria for Measurement Data

The data quality objectives (DQO) process as described in the USEPA Region 5 QAPP Instructions document is intended to provide a "logical framework" for planning field investigations. The following sections address in turn each of the seven sequential steps in the Region 5 QAPP DQO process.

Step 1: Problem Statement

Sediments in the Borrow Pit Lake contain mercury. The sampling and analysis program is intended to document the distribution and concentration of total and methyl mercury in the Lake, and, if deemed necessary following review of the data and discussions with the USEPA Remedial Project Manager, to support risk assessment activities.

Step 2: Decision Identification

The initial use of the data is descriptive (distribution and concentration), and there is no decision point for the descriptive application. Subsequent to review of the descriptive information, a decision will be made as to whether a risk assessment is necessary based on the findings of the field investigation. The decision in this case is to determine whether or not a risk assessment is warranted based on the distribution and concentrations of total and methyl mercury.

Step 3: Identifying Decision Inputs

Decision inputs incorporate both concentration and distribution, and no specific criterion is available for either. The decision will be taken as a result of discussions among Solutia and the USEPA Region 5 Remedial Project Manager. However, a fundamental basis for decision making is that a sufficient number of data points be available from the field investigation to support the discussions. Thus, the necessary input for the decision is the proportion of non-rejected (usable) data points.

Step 4: Defining Study Boundaries

Study boundaries encompass the BPL sediments and have been developed as a result of intensive discussions between USEPA and Solutia.

Step 5: Developing a Decision Rule

As the primary purpose of the data collection is descriptive, and the ultimate decision whether or not to undertake a risk assessment will be based on discussions among USEPA and Solutia, no decision rule can be specified for the overall study objectives. However, regarding the specific decision input (proportion of non-rejected data, proportion), a decision rule can be devised. Given the large number of samples being collected, some nominal loss of data will not hinder description of the distribution of mercury or decisions regarding the need for risk assessment. Given this, a reasonable decision rule would be that 80% of the data points not be rejected for QA/QC reasons.

Step 6: Limits on Decision Errors

Specifications for this step call for 1) giving forethought to corrective actions to improve data usability; and 2) understanding the representative nature of the sampling design. This QA/SAPP meets both specifications for this step. Corrective actions are described elsewhere in the document and in appended contractor and laboratory quality management plans. The representative nature of the sampling design has been assured by discussions among Solutia and USEPA.

Step 7: Design Optimization

In discussions regarding sampling design, USEPA and Solutia considered previous data, data quality objectives, and overall project goals, in keeping with the provisions of this step. In addition, application of the specific decision rules will assure that the findings of the field sampling program are relevant and useful for the specified project purposes.

4.1 Data Categories

Three data categories have been defined to address various analytical data uses and the associated QA/QC effort and methods required to achieve the desired levels of quality. These categories are:

Screening Data: Screening data affords a quick assessment of site characteristics or conditions. This objective for data quality is applicable to data collection activities that involve rapid, non-rigorous methods of analysis and quality assurance. This objective is generally applied to physical and/or chemical properties of samples, degree of contamination relative to concentration differences, and preliminary health and safety assessment.

Screening Data with Definitive Confirmation: Screening data allows rapid identification and quantitation, although the quantitation can be relatively imprecise. This objective for data quality is available for data collection activities that require qualitative and/or quantitative verification of a select portion of sample findings (10 percent or more). This objective can also be used to verify less rigorous laboratory-based methods.

Definitive Data: Definitive data are generated using analytical methods, such as approved USEPA reference methods. Data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce raw data (e.g., chromatograms, spectra, digital values) in the form of paper printouts or computer-generated electronic files.

It is anticipated that both the screening and definitive data categories will be used during the investigation. Field parameters (i.e., turbidity, conductivity, temperature, and pH) that will be obtained during surface water sampling to qualitatively interpret other site data will be determined using screening techniques. All remaining parameters will be determined using definitive techniques.

For this project, three levels of data reporting have been defined. They are as follows:

Level 1 - Minimal Reporting: Minimal or "results only" reporting is used for analyses which, either due to their nature (i.e., field monitoring) or the intended data use (i.e., preliminary screening), do not generate or require extensive supporting documentation.

Level 2 - Modified Reporting: Modified reporting is used for analyses which are performed following standard USEPA-approved methods and QA/QC protocols. Based on the intended data use, modified reporting may require some supporting documentation but not, however, full "CLP-type" reporting.

Level 3 - Full Reporting: Full "CLP-type" reporting is used for those analyses which, based on the intended data use, require full documentation.

The reporting levels for the individual sampling tasks described herein are presented in the following subsections.

4.1.1 Surface Sediment Characterization

Data Use

The sample data will be used for site characterization.

Data Type

Water depth, sediment thickness, and survey data will be collected for all samples. In addition, samples will be collected for laboratory analysis of total and methyl mercury.

Data Quantity

The sample quantities and parametric requirements are summarized in Table 1. Additional information regarding the choice of specific sample collection locations and required analyses can be found in the SRAMP and Section 7 of this document.

Sampling and Analytical Methods

Sampling methods will be as specified in Section 8. The analytical methods are as specified in Section 10. Reporting for total and methyl mercury will be Level 3 (as defined previously).

Measurement Performance Criteria

Precision and accuracy quality control limits for chemical constituents that are used during data review to assess analytical performance are included in Table 2. Quality control limits for field duplicates are also listed in Table 2. Although these quality control limits are only guidelines, frequent failure to meet these limits warrants investigation of the laboratory. Reporting limits are presented in Table 3.

Data representativeness is addressed by the sample quantities and locations identified in the Work Plan. Data comparability is intended to be achieved through the use of standard USEPA-approved methods. Data completeness will be assessed at the conclusion of the analytical activities.

4.1.2 Subsurface Sediment Characterization

Data Use

Subsurface sediment data will be used for site characterization.

Data Type

Subsurface sediment from the odd-numbered grid sections will be submitted for laboratory analysis of total and methyl mercury.

Data Quantity

The sample quantities and parametric requirements are summarized in Table 1. Additional information regarding the choice of specific sample collection locations and required analyses can be found in the SRAMP and Section 7 of this document.

Sampling and Analytical Methods

Sampling methods will be as specified in Section 8. The analytical methods are as specified in Section 10. Reporting for total and methyl mercury will be Level 3 (as defined previously).

Measurement Performance Criteria

Precision and accuracy quality control limits for chemical constituents that are used during data review to assess analytical performance are included in Table 2. Quality control limits for field duplicates are also listed in Table 2. Although these quality control limits are only guidelines, frequent failure to meet these limits warrants investigation of the laboratory. Reporting limits are presented in Table 3.

Data representativeness is addressed by the sample quantities and locations identified in the Work Plan. Data comparability is achieved through the use of standard USEPA-approved methods. Data completeness will be assessed at the conclusion of analytical activities.

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Table 2

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Table 2

Solutia Inc.
Sauget Illinois
Sauget Area 1 - Dead Creek Sediment Removal Action

Analytical Quality Control Limits[a]

Parameter	Field Duplicates RPD	Accuracy - % Recovery		Precision - RPD	
		MS/MSD	Surrogate	MS/MSD	Duplicate[b]
Sediment					
Total Mercury	100	80-120	--	30	--
Methyl Mercury	100	75-125	--	25	--

Notes:

[a] The listed QC limits are based on USEPA guidance and are advisory. However, frequent failures to meet the QC limits warrant investigation of the laboratory

[b] Duplicate control limits apply to laboratory duplicates.

MS Matrix Spike
MSD Matrix Spike Duplicate
RPD Relative Percent Difference

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Table 1

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Table 1

Solutia Inc.
Sauget Illinois
Sauget Area 1 - Dead Creek Sediment Removal Action

Environmental and Quality Control Analyses

Parameter	Estimated Environmental Sample Quality	Field QC Analyses						Laboratory QC Sample						Total
		Trip Blank		Rinse Blank		Field Duplicate		Matrix Spike		Matrix Spike Duplicate		Lab Duplicate		
		Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	
Surface Sediment														
Total Mercury	60	NA	--	1/day	7	1/20	3	2/20	6	2/20	6	NA	--	76
Methyl Mercury	60	NA	--	1/day	7	1/20	3	2/20	6	2/20	6	NA	--	76
Subsurface Sediment														
Total Mercury	30	NA	--	1/day	7	1/20	2	2/20	3	2/20	3	NA	--	43
Methyl Mercury	30	NA	--	1/day	7	1/20	2	2/20	3	2/20	3	NA	--	43

Notes:
1/day One rinse blank per day or one per 20 samples, whichever is more frequent.
Freq Frequency
NA Not Applicable
No. Number
QC Quality Control

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Table 3

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Table 3

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Parameters, Methods and Target Reporting Limits

Analyte	Method[a]	Reporting Limit		
		Sediment	Water	Biota
Total Mercury	7471[a]	0.02 mg/kg	--	--
Methyl Mercury	1630[b]	0.0394 mg/kg	--	--

Notes:

[a] USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste* SW-846 3rd ed. Washington, D.C. 1996.

[b] USEPA. Office of Science and Technology. *Methyl Mercury in Water by Distillation, Aqueous Ethylation, Pugeal Trap, and CVAFS.* EPA-821-R-01-020. 2001

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Sample Containers, Preservation, and Holding Times

Parameter	Method[a]	Bottle Type	Preservation	Holding Time[b]
Sediment				
Total Mercury	SW-846-7471	250 ml plastic or glass jar	Cool to 4°C	28 days to analysis
Methyl Mercury	USEPA 1630	125 ml borosilicate glass jar with Teflon®-lined lid; minimize headspace	Cool to 4°C minimize headspace	48 hours to analysis

Notes:

[a] USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste.* SW-946 3rd ed. Washington, D.C. 1996; and

USEPA. Office of Science and Technology. *Methyl Mercury in Water by Distillation, Aqueous Ethylation, Pugeal Trap, and CVAFS*. EPA-821-R-01-020. 2001

[b] All holding times are measured from date of collection.